UNIVERSAL
LIBRARY

123 527

UNIVERSAL
LIBRARY

IRON AND STEEL DIVISION

1929

TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

IRON AND STEEL DIVISION

1929

PAPERS PRESENTED BEFORE THE DIVISION AT NEW YORK, FEB. 18–20, 1929, AND CLEVELAND, SEPT. 9–13, 1929

NEW YORK, N. Y.
PUBLISHED BY THE INSTITUTE
AT THE OFFICE OF THE SECRETARY
29 WEST 39TH STREET
1929

Notice

This volume is the second of a series constituting the official proceedings of the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers. It contains papers and discussion presented at the New York Meeting, Feb. 18–20, 1929, and the Cleveland Meeting, Sept. 9–13, 1929.

Papers on iron and steel subjects are to be found in many volumes of the TRANSACTIONS of the Institute; during the past 25 years in Vols. 37 to 45, inclusive, 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive, 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS may be found by consulting the general indexes to Vols. 1 to 35 (1871–1904), Vols. 36 to 55 (1905–1916), and Vols. 56 to 72 (1917–1925), and the indexes in Vols. 73 (1926) and 75 (1927).

The papers and discussion presented before the Iron and Steel Division at New York, Feb. 20–23, 1928, and at the joint meeting of the Institute of Metals Division and the American Society for Steel Treating, Philadelphia, Oct. 10, 1928, are in IRON AND STEEL TECHNOLOGY IN 1928, A. I. M. E.

COPYRIGHT, 1929, BY THE
AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS
[INCORPORATED]

PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

CONTENTS

PAGE

INSTITUTE OFFICERS 4

IRON AND STEEL DIVISION OFFICERS AND COMMITTEES 4

FOREWORD 5

PAPERS

Foreign Iron Ores. By CHARLES HART (With Discussion) 7

Iron-ore Sinter. By G. M. SCHWARTZ (With Discussion) 39

Manganese Ore by the Bradley Process. By CARL ZAPFFE (With Discussion) . 68

Gas-solid Contact in the Shaft of a 700-ton Blast Furnace. By S. P. KINNEY and C. C. FURNAS (With Discussion) 84

Blast Furnace Filling and Size Segregation. By C. C. FURNAS and T. L. JOSEPH (With Discussion) 98

Effect of Barium Oxide on the Desulfurizing Power of Blast-furnace Slags. By C. E. WOOD and T. L. JOSEPH (With Discussion) 126

Metallic Electrodes for Cast-iron Welding. By SHUN-ICHI SATOH (With Discussion) 144

Supplementary Notes on Metallic Electrodes for Cast-iron Arc Welding. By SHUN-ICHI SATOH 161

A New Development in Wrought Iron Manufacture. By JAMES ASTON (With Discussion) 166

Unreduced Oxides in Pig Iron and Their Elimination in the Basic Open-hearth Furnace. By C. H. HERTY, JR. and J. M. GAINES, JR. 179

Basic Open-hearth Yields. By C. D. KING (With Discussion) 197

Physical Chemistry of Steelmaking (Round Table) 233

Open-hearth Operation from the Chemical Viewpoint. By C. H. HERTY, JR. . . . 260

Diffusion of Iron Oxide from Slag to Metal in the Open-hearth Process. By C. H. HERTY, JR. (With Discussion) 284

Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron. By A. B. KINZEL and J. J. EGAN (With Discussion) 304

Pure Iron and Allotropic Transformations. By T. D. YENSEN (With Discussion) 320

The Gamma-alpha Transformation in Pure Iron. By A. SAUVEUR and C. H. CHOU (With Discussion) 350

Change in Microstructure of Iron at the A_3 Transformation Point. By B. A. ROGERS (With Discussion) 370

Studies of Hadfield's Manganese Steel with the High-power Microscope (Howe Memorial Lecture). By JOHN HOWE HALL 382

Gases Extracted from Iron-carbon Alloys by Vacuum Melting. By N. A. ZIEGLER (With Discussion) 428

Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-nitrogen. By R. S. DEAN, R. O. DAY and J. L. GREGG 446

INDEX 455

A. I. M. E. OFFICERS AND DIRECTORS

For the Year Ending February, 1930

President, FREDERICK W. BRADLEY, San Francisco, Cal.
Past President, E. DEGOLYER, New York, N. Y.
Past President, GEORGE OTIS SMITH, Washington, D. C.
First Vice-president, W. H. BASSETT, Waterbury, Conn.
Treasurer, KARL ELLERS, New York, N. Y.
Secretary, H. FOSTER BAIN, New York, N. Y.
Assistant Secretary, THOMAS T. READ, New York, N. Y.

VICE-PRESIDENTS

HENRY KRUMB, Salt Lake City, Utah.
F. JULIUS FOHS, New York, N. Y.
W. H. BASSETT, Waterbury, Conn.
GEORGE D. BARRON, New York, N. Y.
HENRY A. BUEHLER, St. Louis, Mo.
EDGAR RICKARD, New York, N. Y.

DIRECTORS

FRANK H. CROCKARD, Woodward, Ala.
J. O. ELTON, Salt Lake City, Utah.
DANIEL C. JACKLING, San Francisco, Cal.
DAVID LEVINGER, New York, N. Y.
RICHARD PETERS, JR., Philadelphia, Pa.
HERMAN C. BELLINGER, New York, N. Y.
KARL EILERS, New York, N. Y.
H. G. MOULTON, New York, N. Y.
J. V. W. REYNDERS, New York, N. Y.
ROBERT E. TALLY, Jerome, Ariz.
ERLE V. DAVELER, Butte, Mont.
EUGENE McAULIFFE, Omaha, Neb.
HARVEY S. MUDD, Los Angeles, Cal.
FRANCIS W. PAINE, Boston, Mass.
WILLIAM R. WRIGHT, Chicago, Ill.

Counsel, DOUGLAS, ARMITAGE AND MCCANN, New York, N. Y.

Officers and Committees of the Iron and Steel Division

G. B. WATERHOUSE, *Chairman*

ALEX. L. FEILD, *Vice-Chairman*
R. H. SWEETSER, *Past-Chairman*
RICHARD MOLDENKE, *Vice-Chairman*
BRADLEY STOUGHTON, *Vice-Chairman*

Executive Committee: 1930, H. M. BOYLSTON, JOHN H. HALL, JOHN JOHNSTON; 1931, F. C. LANGENBERG, FRANCIS F. LUCAS, WILLIAM J. PRIESTLEY; 1932, ZAY JEFFRIES, JOHN A. MATHEWS, ALBERT SAUVEUR.

Papers and Programs: A. L. FEILD, *Chairman;* M. A. GROSSMANN, G. B. WATERHOUSE.

Mining and Metallurgy: A. B. KINZEL, *Chairman.*

Ores and Fluxes: C. B. MURRAY, *Chairman;* R. C. ALLEN, C. S. BLAIR, E. W. DAVIS, W. O. HOTCHKISS, E. E. HUNNER, WILLIAM KELLY, F. B. RICHARDS, W. G. SWART, D. E. WOODBRIDGE, CARL ZAPFFE.

Blast Furnace: S. P. KINNEY, *Chairman;* HORACE J. ALLEN, R. W. H. ATCHERSON, H. A. BERG, A. J. BOYNTON, D. T. CROXTON, GEORGE P. HANSEN, T. L. JOSEPH, C. A. MEISSNER, R. S. MCCAFFERY, C. SNELLING ROBINSON, E. P. ROSS, F. H. WILLCOX.

Coke and Other Fuels: WILLIAM H. BLAUVELT, *Chairman;* H. A. BRASSERT, H. E. COOK, D. J. DEMOREST, S. M. MARSHALL, ARTHUR G. MCKEE, HOWARD P. ZELLER.

Manufacture of Wrought Iron: L. E. THOMAS, *Chairman;* GEORGE O. BOOMER, JOHN M. GILLESPIE, LESLIE M. JOHNSTON.

Manufacture of Open Hearth Steel: L. F. REINARTZ, *Chairman;* JAMES J. BOWDEN, C. L. KINNEY, JR., L. B. LINDEMUTH, W. A. MAXWELL, JR.

Manufacture of Bessemer Steel: E. F. KENNEY, *Chairman;* G. L. DANFORTH, JR., E. T. MCCLEARY, G. A. REINHARDT, F. N. SPELLER, G. B. WATERHOUSE, R. J. WYSOR.

Alloy Steel: A. B. KINZEL, *Chairman;* W. J. MACKENZIE, W. MATHESIUS, J. A. MATHEWS, ALLEN D. POTTS, EARL SMITH, BRADLEY STOUGHTON, JEROME STRAUSS, CHARLES MCKNIGHT.

Electric Furnace Steel: JOHN HOWE HALL, *Chairman;* R. L. BALDWIN, F. E. CLARK, M. A. GROSSMANN, CHARLES MCKNIGHT, THOMAS HARDY.

Cast Iron Foundry: RICHARD MOLDENKE, *Chairman;* JOHN W. BOLTON, HYMAN BORNSTEIN, R. F. HARRINGTON, ROBERT JOB, ROBERT E. KENNEDY, HENRY M. LANE, J. T. MACKENZIE, WALTER M. SAUNDERS.

Steel Foundry: ARTHUR H. JAMESON, *Chairman;* W. J. CORBETT, JOHN HOWE HALL, C. F. PASCOE.

Mechanical Treatment: F. W. WOOD, *Chairman;* D. EPPELSHEIMER, E. C. SMITH, A. A. STEVENSON.

Metallography: H. M. BOYLSTON, *Chairman;* EGDAR C. BAIN, WILLIAM CAMPBELL, F. B. FOLEY, R. O. GRIFFIS, ZAY JEFFRIES, V. N. KRIVOBOK, F. C. LANGENBERG, F. F. LUCAS, W. E. RUDER, ANCEL ST. JOHN, HAAKON STYRI.

Physical Chemistry of Steelmaking: C. H. HERTY, JR., *Chairman;* A. L. FEILD, JOHN JOHNSTON, C. D. KING, A. B. KINZEL, R. S. MCCAFFERY, W. J. MCCAUGHEY, C. E. MEISSNER, L. F. REINARTZ, R. B. SOSMAN, G. B. WATERHOUSE.

Heat Treatment: L. B. MILLER, *Chairman;* ROBERT S. ARCHER, EDGAR C. BAIN, L. A. DANSE, ALBERT DEMMLER, TRUMAN S. FULLER, M. A. GROSSMANN, OSCAR E. HARDER, HORACE C. KNERR, VINCENT T. MALCOLM, D. J. MCADAM, JR., WILLIAM J. MERTEN, J. H. NEAD, FRANK T. SISCO, DU RAY SMITH.

FOREWORD

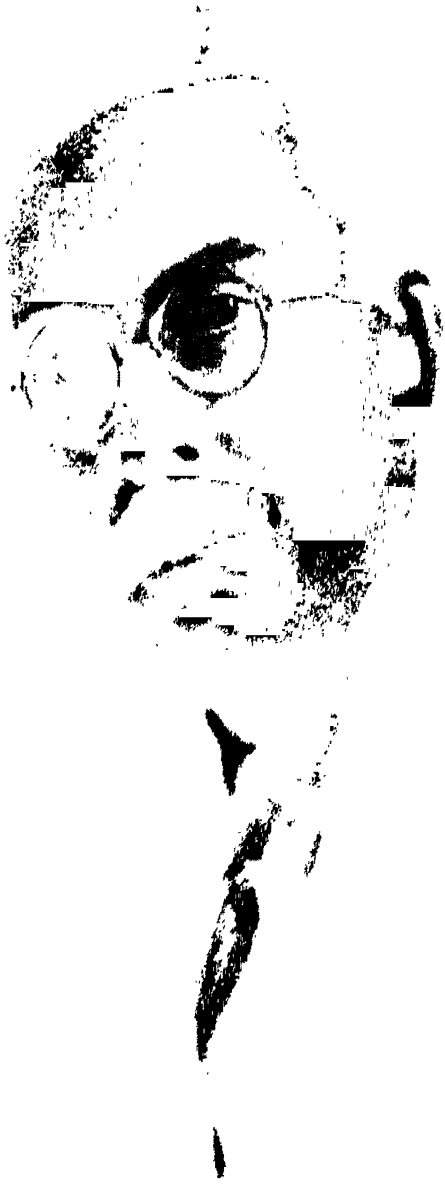
It is a great pleasure, as Chairman of the Iron and Steel Division, to write a foreword to the present volume. We are proud of it as it represents some of the activities during our second year as a separate and coherent Division of the Institute. It was somewhat of an experiment to hold meetings in September but the Executive Committee gave its approval and three very successful sessions were held at Cleveland, Ohio, during National Metal Congress.

In addition to the Henry M. Howe Memorial Lecture by John Howe Hall, which was delivered February, 1929, the volume contains most of the papers presented at the February and September meetings of the Division. An attempt has been made to arrange the papers in order starting with the raw materials, following with blast furnace practice, then with steelmaking and the manufacture of wrought iron and finally bringing together the papers on metallography or physical metallurgy.

The unanimous report of the Robert W. Hunt Committee was to recommend the award of the Hunt Medal to James Aston for the work partly represented by his excellent paper on "A New Development in Wrought Iron Manufacture," presented in this volume and there are numerous other papers that I am sure will prove to be of permanent interest and value.

It is our hope and endeavor that the worthy traditions of the Institute in regard to meetings and papers of importance dealing with iron and steel subjects may be kept alive by the activities of our Division. I would call especial attention to the fact that in 1932 the Division is to have the honor of being one of the hosts welcoming the Iron and Steel Institute of Great Britain when that body visits America.

G. B. WATERHOUSE,
Chairman, Iron and Steel Division, 1929.



JOHN HOWE HALL

Henry Marion Howe Memorial Lecturer, 1929

Foreign Iron Ores

By Charles Hart,* Chester, Pa.

(Cleveland Meeting, September, 1929)

In this paper it is the author's intention to show the extent and character of foreign ores now known to be available; these deposits may be in active production or held in reserve until economic conditions may make them active. He hopes to show the relation existing between these ores and the American supply, and which of the former are now producing or will in turn come into production when our better ores have been exhausted. This phase of this discussion must of necessity include some data as to the present rate of consumption and a study of the changes we may expect here and abroad in the general steel trade and its sources of supply in raw materials. It is obvious that the occurrence of coal, ore and limestone in relation to one another and the proximity of a market are the elements in control of this feature of the problem. If the foregoing situation is favorable, all the other questions may be solved, for it is clear that with proper basic conditions finance, labor and operations will fall in line.

We present a short outline of the present methods of carrying on the foreign iron ore trade, believing that it is of general interest in comparison with our own highly specialized methods, and that with the exhaustion of our better ores we will be compelled to seek a part of our supply abroad.

A partial list of iron ores, with incomplete analyses (Table 1), is added, to give a better understanding of the general situation and explain to some extent the reason for things being as they are in the iron and steel trade of the world and to help in bringing this paper to an informing conclusion. The question of the world supply of iron ores has been a subject for study on the part of geologists and engineers for many years, and found its best results in the Eleventh International Geological Congress, appropriately held at Stockholm, Sweden, in 1910. The proceedings are published in two volumes and are undoubtedly the best records available on this subject at the date of publication. It should be borne in mind, however, that much has happened in the 20 years since these figures were assembled. There is just as much known ore at present as at that time, minus the quantity consumed, plus newly discovered reserves. The World War had great effect upon this situation; during that time explorations were greatly reduced and the settlements after the

* President, Delaware River Steel Co., Chester, Pa.

TABLE 1.—*Analyses of Iron Ores**

Samples Dried at 212° F.

Anal. No.	District	Fe, Per Cent.	P, Per Cent.	SiO_2, Per Cent.	Al_2O_3, Per Cent.	CaO, Per Cent.	MgO, Per Cent.	Mn, Per Cent.	S, Per Cent.	Cu, Per Cent.	Cr, Per Cent.	Ni and Co, Per Cent.	TiO_2, Per Cent.	Loss on Ignition, Per Cent.	Natural Moisture, Per Cent.
	NORTH AMERICA														
	UNITED STATES														
	Lake Superior														
1	Marquette	55.82	0.114	12.79	2.22	1.09	0.78	0.32						2.71	8.31
2	Menominee	55.00	0.426	7.33	2.92	1.78	1.79	0.91						5.37	8.33
3	Gogebic	60.07	0.070	6.82	1.86	0.30	0.26	1.14						3.40	11.77
4	Vermilion	61.47	0.041	7.44	2.86	0.21	0.14	0.08						1.26	6.08
5	Mesabi	58.09	0.064	8.13	2.12	0.25	0.20	0.61						5.20	11.06
6	Mayville	44.85	1.19	5.18	4.42	6.13	3.28	0.08						13.37	10.48
7	Baraboo	53.84	0.070	13.61	4.82	0.10	0.10	0.35						2.17	11.54
8	Cuyuna	52.21	0.233	7.40	3.14	0.53	0.24	3.89						7.64	11.51
9	E. Mesabi (Concentrate)	61.00	0.029	15.00	0.67	0.10	0.50	0.20	0.001				0.03	None	None
10	E. Mesabi (Sinter)	64.00	0.027	9.00	0.67	0.10	0.50	0.20	0.002				0.03	None	None
	Eastern District														
11	Richards	52.61	0.77	13.74	1.44	3.52	1.68	Trace	0.033						1.97
12	Oxford	59.50	0.45	7.50	1.50	2.25	0.35	Trace	0.350	Trace			0.15		0.35
13	Mt. Hope (Concentrate)	58.75	0.500	8.00	1.40	2.00	1.50	0.10	0.040				0.25		0.50
14	Peters	61.20	0.997	4.24	1.33	3.29	0.67	Trace	0.016				0.94		1.40
15	Lyon Moutain	34.20	0.016	35.07	5.66	5.38	2.29	0.08	0.531				0.52	0.25	None
16	Lyon Mountain (Concentrate)	62.87	0.009	8.44	1.13	1.05	0.54	0.08	0.022				0.62		None
17	Forest of Dean	62.17	0.687	5.51	2.31	2.86	1.26	0.15	0.034				0.34	0.51	0.20
18	Old Bed	62.75	0.790	5.36	1.30	3.80	0.57	0.09	Trace				0.23		0.05
19	Harmony (Concentrate)	67.47	0.050	4.67	0.80	0.56	0.26	0.05	None				0.40		0.01
20	Harob Sinter	63.35	0.340	7.05	1.72	1.85	0.47	0.08	0.005				0.35		0.50
21	New Bed (Sinter)	67.57	0.012	4.02	1.05	0.46	0.22	0.10	0.005				0.85		0.50
22	Cornwall (Raw)	45.86	0.007	14.67	2.29	2.88	0.64	0.57	2.200	0.380				9.00	8.26
23	Cornwall (Sinter)	50.40	0.009	14.64	3.75	5.04	0.65	0.54	0.300	0.500			None	None	
24	Sanford (Raw)	47.47	0.018	5.18	4.20	0.42	1.86	0.26	0.142	None	0.16	Trace	21.02	1.56	None
25	Sanford (Concentrate)	56.29	0.003	2.26	4.52	0.10	1.48	0.21	0.104	None	0.19	Trace	12.34	1.62	

26	Clinton, N. Y.	37.72	0.556	12.20	5.83	12.81	4.02	0.14	0.121				2.34	18.99	
27	Clinton, N. Y.	45.93	0.700	15.04	3.96	5.21	1.90		0.450						
28	Clinton, Pa.	47.85	0.208	16.40	5.33	0.16	0.04	0.19	None					8.32	
29	Carbonates, Pa. and Ohio (Calcined)	44.80	0.195	18.50	5.75	6.45	1.95	0.70	0.67						None
	Southern District														
30	Brown Ore (Ala.)	48.54	0.38	11.22	3.64	0.84		0.90	0.09					6.00	7.00
31	Red Ore (Hard) (Ala.)	36.87		12.45	3.10	16.70	0.20	0.14	0.04	Trace	Trace	None	0.13		
32	Red Ore (Soft) (Ala.)	49.00	0.350	17.00	3.50			0.20							
33	Gray Ore (Ala.)	43.34	0.410	28.30	4.50	0.53	0.26	1.39	0.004			0.04	0.24	1.30	
34	Red Ore (Hard) (Tenn.)	27.94	0.421	5.39	3.00	26.42	1.73	0.32	0.021				0.12	21.05	5.60
35	Red Ore (Soft) (Tenn.)	58.31	0.542	8.46	4.79	0.44	0.52	0.34	0.021				0.13	0.35	10.10
36	Cranberry (Tenn.)	57.19	None	14.28	1.08	5.18	0.62	0.12	None				0.12	14.20	1.00
	Western District														
37	Union Hill (N. M.)	51.10	0.065	6.00	0.50	2.40	13.40	0.50	0.40	0.40			Trace		
38	Orient (Col.)	48.92	0.071	9.30	0.62	3.75	0.89	1.49	0.040					12.35	10.00
39	Utah	57.72	0.048	7.67	3.61	2.20	1.80	0.20	0.057				0.40	0.60	3.50
40	Texas	46.63	0.170	14.47	8.17			0.70	0.083						
	CANADA														
41	Antikokan	59.85	0.110	8.68	1.51	3.00	2.54	0.11	2.01	0.12		0.11	None	1.00	
42	Helen (Shipments)	36.50	0.023	4.30	2.96	1.10	6.93	1.80	2.14						
43	Moose Mt. Briquettes	63.03	0.028	6.05	0.93	2.00	1.49	0.06	0.014					None	None
44	Helen Mine	27.24	0.102	13.91	3.63	4.34	5.73	1.34	3.35			Trace	0.09	28.36	
45	Moose Mt. (Mine)	36.70		45.20	0.25	1.06	1.59	0.04	0.024						
	NEWFOUNDLAND														
46	Wabana	50.53	0.92	14.60	4.55	2.45	0.57	0.10	0.049	None	None	None	None	2.47	1.49
	CUBA†														
47	Daiquiri	61.18	0.027	9.28	0.86	1.14	0.38	0.13	0.350	0.07	None		0.05	1.85	
48	Laterite	50.34	0.010	3.75	10.00			0.56	0.180		1.40	0.72		10.50	27.50
	MEXICO														
49	El Mamey	66.52	None	4.70	0.08	Trace	Trace	0.06	0.120				0.11		
50	Mercado	62.50	0.50	5.00					0.180						

* Most of the analyses in Table 1 have been acquired by the author over a great many years and he regards them as authentic. They represent shipments of ore from the mines, sampled by competent men and the chemical work done by reputable chemists The sources of these analyses include well-known concerns in Germany, England, Scotland and the United States, and the author believes that such analyses are far more accurate than any others.

The author has also taken a great many average ore analyses from various places and lumped them together in order to show the nature of the ore in reserves reported in the text.

Some of the analyses have been obtained by correspondence with officials in the mines concerned.

† See also analyses Nos. 177 to 183.

TABLE 1.—(*Continued*)

Anal. No.	District	Fe, Per Cent.	P, Per Cent.	SiO_2, Per Cent.	Al_2O_3, Per Cent.	CaO, Per Cent.	MgO, Per Cent.	Mn, Per Cent.	S, Per Cent.	Cu, Per Cent.	Cr, Per Cent.	Ni and Co, Per Cent.	TiO_2, Per Cent.	Loss on Ignition, Per Cent.	Natural Moisture, Per Cent.
	SOUTH AMERICA														
	CHILE														
51	Chilean No. 1	68.05	0.010	1.75	1.35	0.36	0.38	0.08	0.029					None	None
52	Chilean No. 2	58.10	0.098	8.51	2.66	1.33	1.92	0.10	0.008						
	BRAZIL														
53	Itabira	69.21	0.010	0.37	0.28	0.18	0.18	0.16	0.007					0.10	0.12
54	Canga	61.21	0.123	1.49	4.01	0.028	0.05	0.55	0.040					5.84	
55	Hematite-Bedded	67.45	0.036	0.31	1.51	0.060	0.03	0.29	0.017					1.26	
56	Minas Geraes (Average)	67.08	0.051	0.54	1.41	0.030	0.01	0.26	0.012					1.60	1.65
	VENEZUELA														
57	Imataca	65.75	0.060	1.45		0.18	0.18	0.12	0.007						
	GREAT BRITAIN														
	ENGLAND														
	Jurassic														
58	Northampton	36.67	0.805	14.33	8.80	5.12	0.68	0.32	0.140			16.42			15.55
59	S. Lincolnshire	32.94	0.295	13.53	10.39	17.76	0.76	0.28	0.096					25.01	15.09
60	Cleveland	31.87	0.557	19.56	12.67	5.75	3.77	0.45	0.460					28.97	8.71
61	N. Lincolnshire	25.62	0.351	8.72	5.21	21.62	1.11	1.08	0.193					28.61	11.62
	Carboniferous														
62	Yorkshire	30.65	0.232	14.79	6.47	2.58	2.88	0.89	Trace	25.41	0.23	1.11			0.66
63	Derbyshire	27.07	0.778	10.24	5.46	7.23	5.17	1.16	Trace	31.08	1.31	1.23			0.56
64	S. Staffordshire	33.64	0.179	14.65	4.43	2.17	1.23	0.75	0.050	27.43	0.62	1.12			0.43
65	N. Staffordshire	35.84	0.594	6.57	3.69	2.59	1.77	1.76	Trace	31.89	2.07	1.29			0.25
66	Shropshire	37.93	0.169	7.99	3.84	2.48	1.41	0.60	0.030	32.41	0.47	0.71			0.26
67	N. Wales	36.31	0.432	15.67	4.46	3.13	3.43	1.31	Trace	33.06		0.79			0.41
68	S. Wales	30.71	0.231	15.16	6.87	3.42	3.43	0.66	0.277	30.36	0.41	0.76			0.67
	Hematite														
69	Cumberland	64.09	Trace	5.94	0.72	0.90	0.76	0.14	Trace					0.89	0.39
70	Durham	43.89	None	5.89	0.86	4.77	2.22	2.13	Trace					10.77	2.00
	SCOTLAND														
71	Ironstone	33.21	0.366	3.50	2.98	2.01	2.21	0.99	0.510					32.30	
72	Ironstone	33.59	0.820	0.48	0.37	4.53	4.00	0.53	0.810				0.02	38.60	

73	Ironstone	24.12	0.656	10.00	6.43	12.64	3.24	1.21	0.189					29.80	0.31
74	Ironstone	27.09	0.698	11.50	4.50	8.72	1.48	1.14	0.192					28.50	0.47
75	Banton Blackband	40.96	0.280	0.56	0.11	2.75	3.45	0.88	0.062				Trace	33.91	0.09
76	Banton Clayband	34.75	0.420	8.26	4.78	3.75	3.74	0.94	0.020				Trace	28.53	0.42
	IRELAND*														
77	Ore No. 1	51.80	0.004	6.82	4.82	2.07	0.54	0.31	0.071		2.21	0.90	8.17		8.21
78	Blackband	34.16	0.210	8.97	4.96	2.86	1.68	0.56	0.370	29.64	4.34	1.38	0.51		
79	Hematite	50.00	0.017	3.17	13.02	0.20	0.11	0.57	Trace				2.69		
	EUROPE														
	SWEDEN														
80	Captain	70.70	0.200	1.53	0.39	0.75	0.54	0.16	0.012		Trace	Trace	0.55	1.07	
81	Kiruna "B"	68.29	0.055	1.76	0.43	0.52	0.84	0.09	0.017						0.50
82	Kiruna "D"	60.75	1.870	2.29	0.43	5.98	1.26	0.14	0.019						0.50
83	Gellivare "A"	70.26	0.011	0.59	0.60	0.38	0.42	0.06	0.011						0.50
84	Strassa	65.07	0.010	6.44	0.65	0.94	0.75	0.14	0.086						0.50
85	Kallfall (Concentrate)	64.00	0.003	6.00	1.08	0.42	2.40	0.13	0.040				0.09		
	NORWAY														
86	Sydvaranger (Concentrate)	66.25	0 012	6.30	0.44	0.60	0.44		0.012						
87	Lofoten (Concentrate)	67.67	0.008	2.56	0.60	0.67	0.68	0.16	0.090				0 03		
	FRANCE														
	Minette														
88	Gray	41.34	0.667	6.67	4.69	13.53	1.51	0.41	0.04					22.38	9.50
89	Yellow	40.53	0.742	7.13	4.91	13.49	1.65	0.41						21.90	8.70
	Normandy														
90	Hematite	52.38	0.843	8.43	2.72	0.45	0.15	0.24	0.055					10.62	
91	S. Soumont	38.19	0.59	14.40	5.19	2.05	1.15	0.66	0.020					20.20	
92	May	47.38	0.58	13.11	6.45		0.89	0.55	0.030					10.58	
	Brittany														
93	Hematite	48.91	0.42	15.51	1.39	0.16	0.13	0.08	0.03						
94	Magnetite	52.50	2.55	12.60	0.83	5.15	0.10	0.27							
	Pyrenees														
95	Calcined Carbonate	54.30	0.013	4.45	1.24	0.90	0.10	3.49	0.060				0.11	9.79	8.08
96	Hematite	56.21	Trace	2.30	0.25	Trace	Trace	4.21	Trace					11.05	
	GERMANY														
	E. Rhine District														
97	Siegerland (Raw)	36.76	0.009	7.11	1.34	1.02	3.80	6.72	0.054					35.12	
	Lahn-Dill														
98	Red Ore	46.37	0.260	20.26	3.36	5.13	0.46	0.28	0.620					5.76	
99	Brown Ore	46.31	0.165	20.05	2.62	5.15	0.43	0.13	0 242					11.19	

* See also analysis No. 186.

TABLE 1.—(*Continued*)

Anal. No.	District	Fe, Per Cent.	P, Per Cent.	SiO_2, Per Cent.	Al_2O_3, Per Cent.	CaO, Per Cent.	MgO, Per Cent.	Mn, Per Cent.	S, Per Cent.	Cu, Per Cent.	Cr, Per Cent.	Ni and Co, Per Cent.	TiO_2, Per Cent.	Loss on Ignition, Per Cent.	Natural Moisture, Per Cent.
	Weser District														
100	Weser (1)	31.50		7.27	2.78	3.39	7.61							33.08	
101	Weser (2)	28.86	0.433	20.13	4.98	11.02	2.27		0.42					9.76	
102	Ilseder (1)	32.90	1.10	4.40	0.80	17.00	0.60	4.50						20.00	
103	Ilseder (2)	34.40	1.60	7.80	3.70	14.60	0.80	0.80						17.00	
104	Salzgitter	38.70	0.80	20.85	4.15	1.75	0.93	0.40						12.35	
	Harz District														
105	Red Ore	30.93	0.133	1.75	0.60	28.15	0.40	0.43						20.80	
106	Brown Ore	47.40	0.412	16.51	3.05	0.73	0.66	0.57						9.67	
107	Magnetite	49.80	0.135	19.74	0.90	1.15	0.47	0.47						5.52	
108	Wurttemberg	38.86	0.279	28.18	5.58	1.52	1.14	0.31						6.87	
109	Bavaria	41.07	0.336	22.29	5.43	0.11	0.48	0.84	0.034					10.49	
110	Thuringia	37.65	0.135	14.85	7.73	0.79	2.07	0.23	0.113					23.57	
	Westphalia														
111	Spathic	40.76	0.434	1.93	1.94	2.07	2.91	0.61	0.091					36.91	
112	Carboniferous	32.28	0.319	6.62	4.52	1.66	1.60	0.65	0.266					41.05	
	AUSTRIA														
113	Erzberg (Raw)	38.73	0.015	4.08	1.26	5.92	4.06	2.45	0.079					28.46	
114	Erzberg (Calcined)	50.68	0.025	8.19	1.61	6.19	4.14	3.00	0.169					2.78	
	BELGIUM														
115	Hematite (Average)	35.25	0.425	19.00	9.50	5.65	1.75	0.61	0.150					8.13	
116	Calcareous	25.40	0.440	6.50	3.50	16.00	6.00	2.52	0.500					23.60	
	BULGARIA														
117	Magnetite (1)	60.94	0.006	1.62				0.47							
118	Magnetite (2)	40.00	0.046	31.10		8.90		1.50	0.04						
	GREECE*														
119	Seriphos	52.01	0.037	8.90	1.65	2.03	0.59	1.05	0.201	Trace			0.01	10.15	6.10
	LUXEMBURG														
120	Approximate Average	37.99	0.656	12.97	5.18	11.26	1.09	0.44	0.048					19.67	8.50
	RUSSIA														
121	South Russia (Ural)	62.17	0.039	6.62	1.76	0.65	0.19	0.040	Trace					2.11	
122	Gora Blagodat	58.64	0.036	10.15	4.27	4.86	0.31	0.74	0.015	1.09				0.75	

123	Malia Blagodat	61.76	0.090	5.42	3.75	1.57	1.74	1.12	0.020					
124	Gora Myssokaja	53.13	0.119	15.29	4.55	1.49	0.73	0.72	0.019				1.03	
	CENTRAL RUSSIA													
125	Spathic No. 1	39.73	0.139	2.00	0.80	3.00	1.20	1.96					38.30	
126	Spathic No. 2	39.40	0.138	17.22	2.59	1.20	0.93	0.57	0.30					
	SPAIN													
	Bay of Biscay													
127	Best Spathic	56.09	0.010	8.65	1.85	2.00	3.96	1.00	0.454				0.70	1.00
128	Best Rubio	53.49	0.025	9.10	0.86	1.10	0.84	0.84	0.035				11.31	8.78
129	Santander	47.01	0.026	9.40	1.18	1.13	0.38	0.94	0.062				9.90	10.50
	Mediterranean													
130	Alquife	52.50	0.014	5.00	0.75	5.30	0.66	1.63	0.035				10.60	6.00
131	Rio Tinto	59.23	0.071	10.10	1.90	0.30	0.18	0.07	0.531				7.00	6.20
132	Porman	50.80	0.029	11.70	2.06	0.65	0.11	0.74	0.260				9.10	
133	Teruel	54.05	0.035	4.80	1.23	0.30	0.70	1.72	0.010				12.92	10.50
134	Sagunto Rubio	53.00	0.100	9.17	1.31	0.22	0.81	1.52	0.016				10.00	10.00
	AFRICA†													
	MOROCCO										As. Per			
135	Rif	64.10	0.025	4.35	0.68	0.20	0.18	0.18	0.113	0.03	Cent.		2.59	0.50
136	Navarette	55.50	0.022	11.10	1.65	3.10	0.69	0.40	0.049	Trace	Trace		3.79	
	ALGERIA													
137	Timezrit	58.50	0.014	3.80	0.54	0.62	0.32	1.10	0.010	Trace	Trace		9.35	8.00
138	Ouenza	56.19	0.006	1.67	0.79	4.85	0.67	1.90	0.085	0.05	0.012		8.82	
139	Zaccar	52.65	0.020	4.05	0.90	5.80	0.41	1.40	0.037	Trace	0.012		11.10	11.75
140	Tafna	58.90	0.028	4.50	1.06	2.58	0.62	1.55	0.050				5.45	9.00
141	Rouina "B"	54.64	0.033	11.30	0.71	1.45	0.23	0.21	0.034	None	0.262		7.15	2.17
142	Sebabna	49.10	0.071	7.10	0.99	3.00	0.69	6.25	0.108	0.004	0.012		9.20	
	TUNISIA													
143	Douaria	58.54	0.029	4.95	1.00	0.15	0.06	Trace	0.089	None	0.400		8.20	7.40
144	Djerissa Slata	55.00	0.013	1.35	0.44	4.13	2.05	2.32	0.008	Trace			9.40	
	EGYPT													
145	Sinai	29.85	0.121	3.18	1.83	6.00	0.24	28.46	0.414					
146	SWAZILAND (1)	41.36	0.040	32.81	3.76	1.03	0.69	2.42				None	1.00	
147	SWAZILAND (2)	57.65	0.193	4.39	3.49	1.10	1.84					None	5.99	
148	RHODESIA	49.79	None	13.49	3.10	0.23	None	None	None			10.80		0.86

* See also analyses Nos. 173 to 176.

† See also analysis No. 188.

TABLE 1.—(*Continued*)

Anal. No.	District	Fe, Per Cent.	P, Per Cent.	SiO_2, Per Cent.	Al_2O_3, Per Cent.	CaO, Per Cent.	MgO, Per Cent.	Mn, Per Cent.	S, Per Cent.	Cu, Per Cent.	Cr, Per Cent.	Ni and Co, Per Cent.	TiO_2, Per Cent.	Loss on Ignition, Per Cent.	Natural Moisture, Per Cent.
	ASIA														
	CHINA														
149	Tai-Yang (1)	53.88	0.252	4.67	3.46	2.21	Trace	0.36	0.074					11.57	
150	Tai-Yang (2)	45.50	0.484	11.15	6.42	5.50	0.25	0.33	0.016					9.75	
151	Chihli	30.00	0.050	52.00					0.040						
152	Fengtien	33.05	0.050	49.88					0.100						
153	All China (Average)	54.95	0.160	13.70					0.120						
	JAPAN														
154	Magnetites	63.03	0.030	5.72				0.21	7.37	0.131					
154a	Micaceous	57.55	0.022	12.94				1.03	0.052	0.025					
155	Red Ores	44.03	0.316	19.78				3.99	0.021	0.021					
156	Brown Ores	55.27	0.009	3.09				0.14	0.380	0.010				13.13	
	PHILIPPINE ISLANDS*														
157	Magnetite	63.14	0.056	5.51	4.20	0.25	1.02	0.12	0.14				0.23	None	0.10
158	Hematite	51.72	0.161	9.52	5.43	0.38	0.58	0.31	0.01					0.53	0.27
	BRITISH INDIA														
159	Mayurbhanji	60.18	0.082	4.17	3.60	1.00	Trace						0.32	5.01	
160	Bengal	64.00	0.050	2.10	1.25	0.15	0.18	0.03	0.002						
161	Mysore	58.37	0.057	0.77	9.82	0.13	0.26	0.06	0.047					6.00	0.36
162	Mysore (Titaniferous)	56.83	None	0.88	1.79	0.72	1.58	0.39	0.049		1.59		11.60		
	SIBERIA														
163	Eastern Siberia	53.80		14.62	2.74			2.39							
	AUSTRALIA†														
164	Broken Hill	62.83	0.058	2.93	2.57	0.34	0.21	0.88	0.019	0.004	0.003	0.002	0.18	2.55	
165	Broken Hill (Manganiferous)	48.63	0.054	0.80		1.46	Trace	17.12	0.039	0.029	None	None			6.00
166	New South Wales	55.80	0.172	7.45	1.49	0.25		0.54	0.055				None	8.72	1.25
167	Queensland	62.00	0.110	8.90	2.00	Trace	Trace	Trace	0.110				None		0.10
168	West Australia	68.27	0.009	0.52	2.37	0.06	0.03	0.01	0.010				0.18	0.02	
169	Tasmania	63.48	0.036	7.48	1.19	0.13	0.03	0.02	0.024	Trace	None		0.03	0.43	0.15

	NEW ZEALAND														
170	Parapara	51.38	0.150	9.56	3.36	0.51	0.10	0.51	0.080				0.63	11.84	
171	Onokaka	50.72	0.121	11.55	2.89	0.31	0.13	0.54	0.280					10.28	
172	Iron Sand	57.13	0.250	4.60	2.52	1.53	2.63	0.64	0.010				9.40	0.22	
	LATERITE ORES														
	GREECE														
173	Sokoris Ore	47.65	0.013	7.40	13.75	0.20	0.74	0.36	0.026	0.014	2.42	0.50		5.05	3.53
174	Tsouka Ore	52.30	0.011	6.65	6.80	0.48	1.26	0.39	0.037	0.021	2.07	0.70		9.90	5.58
175	Skyros Ore	46.20	0.030	11.20	9.49	0.62	3.23	0.29	0.021	0.003	2.32	1.14	0.33	5.21	
176	Lutzi	50.00	0.007	9.89	5.40	0.92	2.41	0.21	0.051		2.80	0.15		5.41	
	CUBA														
177	Mayari	48.01	0.010	2.35	9.18						2.26			13.30	
178	Moa	46.22	0.011	3.73	12.23										
179	San Felipe	45.18	0.100	6.75		2.00			0.063		1.70	0.53		12.00	
180	Buena Vista	44.00	0.006	1.62	11.61	1.66		0.91	0.332		1.42	0.76		19.18	
181	Taco	46.23	0.021	2.06	2.16						2.07				
182	Navas	42.48	0.032	3.01	6.12						2.39				
183	Mayari	50.34	0.010	3.75	10.00			0.64	0.180		1.40	0.72		10.50	27.50
	PHILIPPINE ISLANDS														
184	Surigos	54.29	Trace	1.04	10.56				Trace			None		6.60	13.50
185	Surigos (Average)	47.40													12.87
	IRELAND														
186	Laterite	34.00	12.000		12.00								5.00	10.00	
	NEW SOUTH WALES														
187	Basaltic	30.21	0.241	33.03	7.76	0.58	0.32	0.80	Trace			Trace	Trace	10.27	3.03
	AFRICA														
188	Nigeria	47.30	0.051	10.58	9.16	0.61	0.26	0.02	0.080				1.62	8.77	0.86

* See also analyses Nos. 184 and 185.

† See also analysis No. 187.

war so changed the geography of the world that although the total reserves are essentially the same their national distribution is far different. In the year 1922, a further complete survey was made by the Imperial Mineral Resources Bureau published in eight volumes,[1] and naturally the British territory finds separate places in these works. In the meantime, various geologists have done field work on the foreign ore supplies and it is their reports that give authority to most of our later compilations; we refer to them by name on account of the excellence of their work: Weld's results on India and Cuba, Roesler on Europe, Eckel on Labrador and the United States, T. T. Read and Tegengren on China, Derby, Leith and Harder on Brazil, Bain in the Far East, together with many others of like value. We mention these to give authenticity to our figures and to absolve ourselves from any appearance of originality in the presentation of their data.

Primarily, this paper discusses foreign ores especially in regard to their effect on our own industry. A cursory examination of the world's supply is necessary so that this problem may be intelligently studied. The 1910 Stockholm figures placed the known world supply at 22,409,000,000 tons with an additional potential reserve of 123,377,000,000 tons. The latter did not include the enormous reserves of Africa and a careful survey of the situation in 1919 placed the known and potential ore reserves of the world at 131,708,000,000 tons[2] and of this amount 100,000,000,000 tons[3] or 76 per cent. of the entire world reserves were credited to the United States.

North America

United States

The Lake Superior ranges may be considered as our greatest reserve, and, in fact, form one of the six great reserves of the world.

The principal ranges and the year in which they came into production, together with shipments to date, are embodied in Table 2.[4]

A careful estimate by M. C. Lake[5] placed the total Lake Superior reserves as of 1927 at 1,510,437,621 tons, 81 per cent. of which was on the Mesabi Range. It is presumed that this figure includes only merchantable ore as shipped in accordance with our present practice. It does not include 72,000,000,000 tons[6,7] of possible and probable ore in this

[1] Iron Ore. Imperial Mineral Resources Bureau, London, 1922. Pts: I to VIII.

[2,3,4,6] Figures taken from what the author considers reliable sources.

[5] The Iron Ores of Lake Superior, 6th ed. Crowell & Murray, Inc., Cleveland, 1927.

[7] Dr. C. W. Hayes, Chief Geologist, U. S. Geological Survey, in his estimate of 1908 credited the Lake Superior district with reserves of 72,030,000,000 tons of iron ore described as "not available;" his totals for the United States were 75,116,070,000 tons not available and 4,788,150,000 tons available. See E. C. Eckel: Iron Ores. Their Occurrence, Valuation and Control, 346. McGraw-Hill Book Co., Inc., New York, 1914.

TABLE 2.—*Production of Ore, Lake Superior Ranges*

Range	Analysis*	Year	Production to Jan. 1, 1929, Tons
Marquette	1	1854	164,504,672
Menominee	2	1877	162,680,437
Gogebic	3	1884	173,638,254
Vermilion	4	1884	54,770,022
Mesabi	5	1892	815,686,695
Mayville	6	1892	3,022,698
Baraboo	7	1904	
Cuyuna	8	1911	27,197,945
Total			1,401,500,723

* Numerals refer to analyses in Table 1.

district, to which should be added 3,008,352,328 tons[8] of ore immediately available. The potential reserve of 72,000,000,000 tons of lean ore awaits its turn and is subject to beneficiation and use under conditions more exacting than now hold in the world's furnace practice today.

Alabama District.—The next region in importance in the United States is that centering in Birmingham, Alabama, which, on account of the proximity of good coal and fluxing stone, is now second only to the Superior district and is becoming increasingly important each year. The reserve may be roughly estimated as follows: Brown ore (anal. 30),[9] 29,250,000 tons;[10] red ore (anal. 31), 355,000,000 tons; gray ore (anal. 33), 27,500,000 tons; total, 411,750,000 tons. The brown ore is limonitic and in this discussion we will follow Eckel in that all limonites are brown ores but that all brown ores are not limonites. The red ores were originally hard (anal. 31) due to lime, but weathering at the surface lowered the lime content and automatically increased the iron and silica content and gave the soft red ore (anal. 32).

As to the magnetites of the United States there are immediately available in the Eastern part (anal. 11 to 25, inclusive) a reserve tonnage in excess of 210,000,000 tons[11] of which 40 per cent. is titaniferous. To this there might be added 140,000,000 tons[12] as possible or probable, 70 per cent. being of a titaniferous nature. There are additional deposits of magnetic ores in the Lake Superior district, a part of the vast potential reserves of that territory, placed at 4,500,000,000 tons[13] nontitaniferous and 25,000,000 tons[14] carrying titanium. The brown and red ores centering in Tennessee (anal. 34) amount to more than 600,000,000 tons[15] and may be considered a reserve of the greatest importance and will be workable under future conditions. Reliable estimates give to the

[9] Indicates number of analysis in Table 1.

[8,10,11,12,14] Figures taken from what the author considers reliable sources.

[13,15] E. C. Eckel: Iron Ores. Their Occurrence, Valuation and Control. McGraw-Hill Book Co., Inc., New York, 1914.

territory west of the Mississippi River a total of 1,097,300,000 tons[16] as of the year 1919, one-third of which is now available and the balance constitutes a potential reserve. Most of it lies in Texas (anal. 40), although Utah (anal. 39) may lay claim to 40,000,000 tons. The siderites (anal. 29) of Ohio and Eastern Pennsylvania are of interest in that they are akin to England's greatest reserve and that they are not now in production, because an abundance of Lake Superior ore is obtainable on a more profitable basis. America's black-band ores exceed 300,000,000 tons[17] with probably not more than 75,000,000 tons of metallic iron.

Canada

This great territory adds little to the known reserves of Great Britain. It has been the subject of recent study on the part of the Canadian Government as shown in a report published in 1923.[18] This report and other sources of information show that there is little ore of workable quality in Canada, although total reserves for the Dominion are placed at 300,000,000 tons,[19] 80 per cent. of which must be beneficiated. This condition is emphasized by the fact that Canada's average importation of iron ore from the United States and Newfoundland over the last 5 years has been at the rate of 1,401,727 tons[20] against an average home production per year of only 1774 tons.[21] A study of their ores makes full explanation of this condition; all require preparation in one way or another as reference to their analysis will indicate. The Antikokan (anal. 41) is high in sulfur, the Helen (anal. 44) a very low iron siderite, and the Moose Mountain magnetite (anal. 45) rather refractory. The Moose Mountain briquettes (anal. 43), however, are of excellent quality. All the methods of beneficiation suitable to these operations are expensive, with the result that the importations cited above are quite as might be expected.

Newfoundland

On Bell Isle in this province occurs an outcropping of another of the six great orebodies; it does not indicate, however, the immense tonnage of ore extending under the sea and which has been opened up for a distance of more than 4 miles and is still in ore. This oolitic ore known as Wabana (anal. 46) is found in seven layers and is now in active production. Last year's shipments aggregated 1,547,893 tons[22] which is a record for this operation. At least 1,000,000 tons went to Germany and the balance to Canada, the United States and England. The reserves are such

[16,17] Figures taken from what the author considers reliable sources.

[18] Report of the Ontario Iron Ore Committee, with Appendix. Toronto, 1923.

[19] Iron Ore. Imperial Mineral Resources Bureau, London, 1922. Pts. I to VIII.

[20–22] Annual statistical report, Bureau of Statistics, Amer. Iron & Steel Inst.

(Table 3) as to make the mine of interest to American smelters because of its location and its possibilities as a future supply, although large shipments to this country do not obtain as an ore of its chemical and physical properties does not blend well with our ores. However, as time goes on it will become one of our greatest sources of iron on account of the location and size of the deposit.

TABLE 3.—*Estimate of Wabana Reserves*

	TONS
J. P. Howley[23]	3,635,000,000
E. E. Ellis[24]	3,500,000,000
R. E. Chambers[25]	3,635,343,360
E. C. Eckel[26]	3,500,000,000

Eckel further states in his book[27] as follows: "If we assume that there is no technical impossibility in the way of working the ore by slopes from the islands or mainland as far out as Cape St. Francis, we have to deal with a reserve aggregating some ten thousand million tons." He further indicates that methods of mining and other conditions places the recoverable ore at 5,000,000,000 tons.

Cuba

This island because of its proximity to the United States and its immense reserves is of intense interest. It contains the third great orebody so far considered, in addition to about 9,000,000 tons[28] of magnetite (anal. 47) to be found on the South side of the island; these two represent practically all of Cuba's reserves. The North Coast ores are laterite (anal. 48) and in their present form are practically useless, although they contain at least 1,000,000,000 tons[29,30] of iron. There is a large tonnage of laterite ore in the world reserves; all of these ores will be discussed in a later paragraph.

Mexico

Two deposits, the Cerro del Mercado (anal. 50) (Iron Mountain) and the El Mamey (anal. 49) embody the more important deposits. Mexico was credited with a total of 242,978,000 tons[31] in reserve in 1918. These, with about 10,000,000 tons of scattered deposits comprise Mexico's reserve, part of which is in active operation.

---

[25] Iron Ore Resources of the World, Eleventh Internat'l Geologic Congress, Stockholm, 1910. (In 2 vol.)

[26,27] E. C. Eckel: *Op. cit.*

[23,24,28,30,31] Iron Ore. Imperial Mineral Resources Bureau, London, 1922. Pts. I to VIII.

[29] J. E. Spurr: Political and Commercial Geology. McGraw-Hill Pub. Co., Inc., New York, 1920.

North America's total ore reserves, actual and potential, may be placed at 114,000,000,000 tons,[32] as against Tegengren's 1910 estimate of 79,362,000,000 tons.[33] The latter estimate does not include a figure for Canada nor any potential figures for Newfoundland, although in both instances Tegengren conceded "enormous reserves."

South America

The ore reserves of South America are of interest in two instances, Chile and Brazil, the former for the reason that the ore is now mined for shipment to the East Coast of America, the latter because it undoubtedly holds the greatest and best orebodies in the world and due to its location will eventually make heavy shipments to us.

Chile

Chilean ore (anal. 51), essentially the same as Tofo, is found in abundance, together with other ores (anal. 52) lower in iron and in some cases self-fluxing. Chilean data are almost entirely due to the early efforts of Vattier, and later and more dependable facts have been obtained by officials of the Bethlehem Steel Corp. which is actively engaged in mining the Tofo ore. It is hoped that production and shipment to America will exceed 1,750,000 tons this year as against an average annual production for the five previous years of 1,350,827 tons.[34] The reserves in Coquimbo province exceed 200,000,000 tons.[35]

Brazil

Brazil holds without doubt another of the six great deposits known to exist, probably the greatest, although recent developments in India may tend to change this situation. Certainly from an American standpoint it is one of the most important, in that it will probably be the first foreign ore to which we will turn to augment our supply when the depletion of our Lake ores becomes a fact.

The state of Minas Geraes is the center of the ore reserves of Brazil and this deposit has been known for years. Recent figures indicate 3,500,000,000 tons[36] of ore in this state alone, with a grand total credited to Brazil of 7,500,000,000 tons[37] of ores of all grades. Outstanding ore beds in Minas Geraes are shown in Table 4.

---

[32] Figures taken from what the author considers a reliable source.

[33] Iron Ore Resources of the World. Eleventh Internat'l Geologic Congress, Stockholm, 1910. (In. 2 vol.)

[34] Annual statistical report, Bureau of Statistics, Amer. Iron & Steel Inst.

[35,36,37] Iron Ore. Imperial Mineral Resources Bureau, London, 1922. Pts. I to VIII.

TABLE 4.—*Outstanding Ore Deposits, Minas Geraes, Brazil*

Name	Iron, Per Cent.	Phosphorus, Per Cent.	Moisture, Per Cent.
Burnier	62.31	0.112	0.90
Sabara	69.26	0.007	
Itabira de Campo	69.06	0.015	

Bedded hematite (anal. 55) is the most important of these deposits. Canga (anal. 54) abounds to the extent of 1,700,000,000 tons.[38] The 1910 Stockholm meeting at which Derby presented his report, called attention to these immense deposits with the result that the best of them were promptly purchased by corporations foreign to Brazil. American capital as of 1919 controlled 580,000,000 tons[39] of this ore as a reserve. The Minas Geraes ores (anal. 56) were partly developed but as yet no shipments of note have been made. Reliable estimates indicate that this ore could be placed at Atlantic seaboard points at a cost of about 10c. per unit, which is in line with prices holding at the present time on foreign ores imported from the regular sources.

Venezuela

A doubly unsuccessful operation in this country developed the mines at the foot of the Imataca Mountain on the Orinoca River. Shipments of this Imataca ore (anal. 57) were made to America in 1912 and some of it smelted in the furnace at Chester, Pa. This is a rich, dense ore, part hematite and part magnetite. Shipping conditions on the river and an apparent deterioration of the ore brought this operation to a close.

As to the other South American countries little is known. Dutch Guiana is believed to have laterite ores in excess of 100,000,000 tons,[40] Uruguay is credited with 80,000,000 tons[41] and Peru with 500,000,000 tons[42] near the sea, and extensive but unmeasured reserves of laterite are known to exist in British Guiana.

As to the total reserves of South America, Eckel[43] places them at the round figure of 8,000,000,000 tons from which we may consider that 500,000,000 tons were known to exist outside of Brazil, as of 1914. More recent surveys however, place this figure as of 1922[44] at 8,490,000,000 tons to which may be added rather large tonnages of unknown potential reserves to the end that 10,000,000,000 tons may be taken as the available ore reserve of South America, although the creditable figure of 8,349,000,000 tons[45] is used in the summary of this paper.

[39,45] Figures taken from what the author considers reliable sources.

[38,40–42,44] Iron Ore. Imperial Mineral Resources Bureau, London, 1922. Pts. I to VIII.

[43] E. C. Eckel: *Op. cit.*

Europe

The steel manufacturers of Europe, especially those operating in England, Germany and France, are America's competitors. The ores available to these countries are therefore of first importance to us. We, in a small way, import European ores and share in a competitive way in the other ores upon which they depend for a supply.

England

The United Kingdom is credited with 2,306,947,000 tons[46] of actual ore as of 1922; with possible additional reserves of 9,447,372,000 tons[47] less an approximate consumption of 55,000,000 tons, the total is 11,699,-319,000 tons. As England imports about one-third of its ore requirements, it is to be expected that much of this reserve is unavailable under present competitive conditions and such is the case, for Table 1 (anal. 58–68 inc.) shows that these ores are low in iron content and need roasting before using in the furnaces. These ores may be considered as siderites, as limestones impregnated by iron, or as ores associated with coal and therefore carrying sufficient carbon to make them self-calcining. These ores are the banded ores and are either blackbands (anal. 75) or clay-bands (anal. 76) as shown in the Scotch Banton ore (anal. 74) and indicates the origin of these classifications.

The hematite ores (anal. 69–70) constitute 130,300,000 tons[48] of England's reserve and in conjunction with importations from Spain and North Africa are the ore mixture used in making England's hematite steel. The ores of Scotland are largely ironstones (anal. 71–74) and in iron content approach the analysis of the English ores. The ores of Ireland (anal. 77–79) are of no significance in this resume.

Germany

Undoubtedly the situation of Germany is of the greatest significance to us in that we may expect from this country the severest competition in iron and steel products both here and abroad. To their methods of business the Germans bring diligence and knowledge, and Germany's proximity to, and partial ownership in another of the great world deposits as well as its abundant supply of fuel, makes this nation a power in iron and steel.

The records indicate immense holdings of ores other than the Minette, and that these may be mixed with the richer ores imported from Sweden and Spain. It is not likely that any of the German ores, as such, will find their place in American mixtures. Roesler[49] places the total German reserves at 1,374,400,000 tons, of which 250,000,000 tons may be considered as actual. The Minette situation has been greatly disturbed by

[46–48] Iron Ore. Imperial Mineral Resources Bureau, London, 1922. Pts. I to VIII.

[49] W. Roesler: Iron Ore Resources of Europe. U. S. Geol. Surv. *Bull.* 706 (1921).

reparations since the war. Pre-war figures indicate that France owned 3,000,000,000 tons[50] and Germany 2,330,000,000[51] tons of the Minette reserve with the addition of Luxemburg and its close German alliance. Germany and France were practically on a parity, but due to reparations practically all of this Minette ore is now creditable to France. Although France has this large tonnage under national control, much of actual ownership is vested in German corporations. The ores of Germany remaining are notable for their low iron content. Reference to the analyses (97–112) shows diversity in other elements. These analyses explain the need of the richer imported ores and the use of Minette available by purchase from Luxemburg and France. The reserve as of 1929 is 1,300,238,526 tons.[52]

Luxemburg

Pre-war conditions developed close commercial relations with Germany, which are reflected in today's situation, in that large tonnages of its Minette ore (anal. 120) are shipped to Germany, although changed political conditions have brought about closer relations with Belgium on account of the latter's coal supply.

These Minette ores are not different from those of France, as in 1921 Roesler used a figure of 270,000,000[53] tons as the reserve. Deducting ore consumed leaves as of 1929, 210,000,000 tons available. This ore is being used at the rate of 7,700,000 tons per year and indicates a 30 years' supply.

France

The Minette ores in French territory, to which reference has been made may be placed at 5,330,000,000 tons.[54] This may be considered as available as of 1922. Roesler places a figure of 7,825,000,000 tons[55] as the actual and potential Minette ore as of 1921 (exclusive of Luxemburg). From this figure we should deduct ore consumed as of 1929, 113,975,322 tons,[56] which places France's present Minette reserve at 7,711,024,678 tons.[57] This tonnage together with all other actual and potential ore, gives a total for France of 9,704,624,678 tons[58] as of 1921, and deducting for consumption the grand total is 9,561,219,054 tons.[59] The Gray Minette (anal. 88) and Yellow Minette (anal. 89) may be taken as representative of these deposits. The Normandy ores (anal. 90–92), together with Brittany hematite (anal. 93) and magnetite (anal. 94), comprise about 225,000,000 tons of actual ore, which with 30,000,000 tons of ore in the Pyrenees, (anal. 95–96)

[50,51] H. Mennig, F. Haeberlin, Ltd.: Personal correspondence, 1926.

[52] Figure taken from what the author considers a reliable source.

[53,55] M. Roesler: *Op. cit.*

[54] Iron Ore. Imperial Mineral Resources Bureau, London, 1922. Pts. I to VIII.

[56] Annual statistical report, Bureau of Statistics, Amer. Iron & Steel Inst.

[57–59] Figures taken from what the author considers reliable sources.

Brittany and Anjou hematite (anal. 93) and magnetite (anal. 94), add 250,000,000 tons to actual reserves, all contributing to France's grand total as shown above.

Sweden

The ores of Sweden are almost entirely magnetic, many of Central and Southern Sweden requiring concentration and agglomeration. In Lapland, however, is the sixth of the great world deposits, in masses of excellent magnetite (anal. 80–83). The author is reliably advised that in one mountain alone 1,700,000,000 tons[60] of this ore is known to exist and the body has not been completely prospected. This figure is presented in spite of the fact that in the 1910[61] conference all Sweden was credited with actual and potential ore reserves of 1,336,000,000 tons and Roesler[62] places Sweden's total at 2,181,700,000 tons. The British Bureau figures for 1922[63] place this tonnage at 2,595,700,000 tons, and deducting the interim consumption of 49,270,461 tons gives the 1929 grand total reserve of Sweden as 2,545,429,539 tons. Because of their richness and accessibility these ores may be considered the best source of merchant ore as there is no great consumptive capacity in Sweden. Sweden's average production for the years 1924 to 1926, inclusive, was 8,766,795 tons.[64] Because of labor troubles, 1928 scarcely exceeded half this figure, but it is hoped that the present year will show record production.

Spain

The shipments from this nation are made from Bilbao in the Bay of Biscay and from several ports on the Mediterranean Sea. In common with Sweden, Spain is a large producer of iron ore but a comparatively small consumer. For more than the 15 years ending just prior to the World War Spain's average annual production was slightly more than 8,000,000 tons, over half of which went to England as it naturally would because of trade conditions and the fact that the ores were hematite in quality and used to complete mixtures of ores of which the English ores were the basis. In no single year did shipments to Germany exceed 1,000,000 tons. The mines of Spain because of their inadaptability to modern methods and machinery have been greatly affected by the generally disorganizing effects of war upon labor. Extraordinary demands for iron this year should establish the ability of Spain to produce ore.

[60] Figures taken from what the author considers reliable sources.

[61] Iron Ore Resources of the World. Eleventh Internat'l Geologic Congress, Stockholm, 1910. (In 2 vol.)

[62] M. Roesler: *Op. cit.*

[63] Iron Ore. Imperial Mineral Resources Bureau, London, 1922. Pts. I to VIII.

[64] Annual statistical report, Bureau of Statistics, Amer. Iron & Steel Inst.

Reference to Table 1 (anal. 127–134) will indicate the excellence of the Spanish ores and their great vogue in England, and because of the triangular situation on coal originating on the Tyne and Tees, the need of ore at these points as well as at Rotterdam for German delivery and coal requirements at Bilbao, the movement of this commodity brought about an ideal shipping situation—cargoes each way, so that it was possible to charter each loading at four shillings or less or double the amount for the round trip. The exchange of commodities was mutually advantageous, particularly as the English furnaces were never very far inland. The principal ores involved were Best Bilbao Spathic and Best Bilbao Rubio, the former calcined and the latter hematite of proper quality. It is of interest that there has been the same deterioration in the iron content of these Rubio ores as in the Lake ores and that it is about equal in percentage. The Mediterranean ores have found a market in England but not as readily as the ores originating at Bilbao. Foreign capital, mostly English controls many Spanish mines.

Spain's total ore was placed at 1,327,500,000 tons by Roesler[65] and a reduction of 28,500,000 tons[66] since 1921, would make this country's reserves 1,299,000,000 tons.[67]

The countries discussed represent the principal ore-producing countries of Europe. Their total reserves as of 1929 may be placed at 26,615,-206,119 tons[68] to which we may add 2,497,335,000 tons[69] from all other countries, giving the continent a known reserve of 29,112,641,119 tons.

Africa

Aside from the North Coast of Africa, the ores found on this continent are unimportant. The Mediterranean ores, however, find a market in the United States and are well known, and come principally from Algeria and Tunisia. The former country produces ore of diversified character, much of which is of low phosphorous content. Timezrit (anal. 137) and Ouenza (anal. 138) are especially good for making low-phosphorus pig iron here as well as in England. Experience shows that Douaria (anal. 143) is one of the best working ores obtainable, and that the Rif ore (anal. 135) from Morocco is worthy of the development now taking place at the mines, in which modern crushing and handling machinery is being installed in the expectation that production will reach 1,000,000 tons per year by 1930. This is a hard hematite and should be crushed to a 2-in. size or less. Excellent manganiferous ore from Egypt finds ready market in this country under the name of Sinai (anal. 145). Reference to other African ore will be made in the paragraph on laterite ores. North Africa is credited with 150,000,000 tons,[70] two-thirds of which lies in

[66–68] Figures taken from what the author considers reliable sources.

[65,69] M. Roesler: *Op. cit.*

[70] Iron Ore. Imperial Mineral Resources Bureau, London, 1922. Pts. I to VIII.

Algeria. The balance of Africa is practically unmeasured, estimates running vaguely from "considerable," through "many thousand million tons" to "enormous."

Asia

British India seems to be the outstanding country of Asia. Because of recent developments in operations India is shipping more pig iron to America than any other foreign country, its own steel industry has developed, and recent discoveries of ore near Calcutta have added immense reserves to the world's supply. The ore will not, at least for many years, be available to American furnaces. Charles P. Perin,[71] than whom there is no greater authority on Indian iron and steel matters, advises that these discoveries of ore represent holdings in excess of 20,000,000,000 tons and within reasonable distance of India's best coal deposits. The ores of this country are of excellent quality and largely laterite, not however to be confused with chromiferous laterites which abound in Cuba. Mayurbhanji (anal. 159) may be taken as representative of the Tata Iron & Steel Co's. ores. Mysore (anal. 161–162) is also a desirable ore. India's reserves were placed at 750,000,000 tons in 1910, however, and it would seem that Perin's 1920 figure is a sufficient reserve for any nation, adding as it does a century of ore consumption based upon the rate now holding in the entire world.

China

Tegengren[72] states that the total reserves of China may be placed at 941,700,000 tons, of which 396,000,000 tons are actual and the balance potential. The entire tonnage has an average iron content of about 40 per cent.; although the contact ores designated in the list (anal. 153) as "All China" contain about 55 per cent. of iron, while the Archean ore averages just under 35 per cent. Tegengren's figures, authorized by the Chinese Government are quoted by Bain[73] but he is not in accord with them and his discussion indicates that he believes these figures represent maximum rather than minimum reserves.

Japan

This country shows only 80,000,000 tons[74] in accredited reserves.

It would seem that all Asia contains, according to the latest reports, ores in excess of 22,000,000,000 tons.

---

[71] C. P. Perin: Recent Developments in the Iron and Steel Industry of India. Yearbook, Amer. Iron & Steel Inst. (1920).

[72] F. R. Tegengren: The Iron Ores and Iron Industry of China. China Geol. Surv. *Mem.* Ser. A, No. 2. Pts. 1, 2 (1921–1924).

[73] H. F. Bain: Ores and Industry in the Far East. Council on Foreign Relations, New York, 1927.

[74] Iron Ore. Imperial Mineral Resources, Bureau London, 1922. Pts. I to VIII.

Australia

These islands contain immense ore reserves, but are too far from America to be pertinent to this discussion; however, one ore, Broken Hill manganiferous (anal. 165), reaches this country as ballast for ships carrying wool. Because of its ore holdings and a desire to develop its industries there is considerable activity in iron and steel in Australia. The total reserves may be placed at 921,678,000 tons,[75] with 69,574,000 tons[76] in New Zealand, or a total of 991,252,000 tons.

The aggregate figures for the continents give a world's supply of 174,602,893,119 tons.[77] The figure for 1919 of 131,704,000,000 tons, previously mentioned, is considerably less. The author's total figure takes into account Perin's estimate of 20,000,000,000 tons of newly discovered ore in India[78] and includes numerous other recent dicoveries. As it does not include any of the reserves estimated as being "enormous" but which are of unknown tonnages, the author feels that his figure approximating 175,000,000,000 tons of ore is under rather than over the world's supply.

The Laterite Ores

Because of their abundance and metallurgical interest the ores in this class are given a separate heading. Normally, these ores are the result of laterization or weathering in humid climates; they occur in profusion in countries having the needed heat and moisture. One trivial deposit occurred in America proper near New York City. It is of no significance here excepting that it did occur. Vast tonnages of laterite ore abound in India from the disintregration of schists and it was this ore which brought about the development of the Tata Companies in India. Laterites are a brown ore and consequently from a chemical standpoint, most desirable. A small amount of laterite ore in Ireland (anal. 186) is of basaltic origin. The high percentage of titanic acid is its distinguishing feature. Geological reports indicate vast tonnages in Africa, due to the disintegration in part of schists and serpentines. These deposits in Sudan and West Africa are reported as being enormous and at many thousand million tons. The Nigeria (anal. 188) is said to be representative of these deposits. The Basaltic (anal. 187) laterites of Australia are of scientific import, but in no way may be considered as a source of supply for this or any other country. The laterite ores of greatest interest to us, however, are the immense deposits in Cuba (anal. 177–183), lesser ores in Greece (anal. 173–176) and Porto Rico, and really important ores in the faraway Philippine Islands (anal. 184–185). These ores are found upon the

[75–76] Iron Ore. Imperial Mineral Resources, Bureau London, 1922. Pts. I to VIII.

[77] Figure taken from what the author considers a reliable source.

[78] C. P. Perin: *Op. cit.*

originating serpentine rock and contain measurable portions of chromium, nickel and cobalt.

The transition from serpentine to ore is worked out by Weld[79] and in the same manner as Sir Thomas Holland showed the changes from dolerite to the laterite ores of India.

The Cuban laterites would make an ideal ore supply for this country when our Eastern ores are exhausted, were it not that they are high in alumina, contain the undesirable elements mentioned above and are of poor physical condition. The iron manufacturers of the Atlantic coast are alive to this situation and practically all of the available ore of this character is owned in the United States. Heavy expenditures for the construction of piers and sintering plants in Cuba were made, but because of unsatisfactory operations and poor furnace practice in the United States, these operations have been reduced to a minimum. Some method of beneficiation must be evolved whereby the metallic iron can be removed from its association with chromium, nickel and alumina and the iron residue satisfactorily agglomerated. Much work has been done along these lines but as yet no tangible results are apparent. The need of such a process is the excuse for the special attention given the Cuban laterite ores, and it is stated unadvisedly that there is no more important metallurgical problem before the American steel industry today, nor one which will be more remunerative, and in announcing this problem no confidences are violated for already four processes have been developed, none of which are commercially successful. This importance must be self-evident as reflected in the size of the deposit, its low mining cost and its proximity to the Atlantic ports.

The characteristics of this ore have been fully discussed in various papers[80] presented to the Institute and a further discussion of its many phases is unnecessary. Deposits in Greece have at times been worked and rather complete analyses are available (Nos. 173 to 176 incl.).

Comparison of analyses of samples dried at 212° F. with like samples of Mayari shows results so close that the originating rocks would seem to be identical. This is further confirmed by the fact that both deposits rest upon serpentine. The Grecian reserves probably are not in excess of 100,000,000[81] tons. These Greek ores are now available for America. They are offered from time to time without sales. The Philippine deposits are nearly identical with these ores, but are too far distant in miles and time to be of any moment.

---

[79] C. M. Weld: The Residual Brown Iron Ores of Cuba. *Trans., A. I. M. E.* (1909) 40, 299.

[80] C. K. Leith and W. J. Mead: Additional Data on Origin of Lateritic Iron Ores of Eastern Cuba. *Trans.*, A. I. M. E. (1915) **53**, 75.

W. E. Pratt: The Iron Ores of the Philippine Islands. *Trans.*, A. I. M. E. (1915) **53**, 90.

[81] M. Roesler: *Op. cit.*

Beneficiation

A study of the various ores discussed in this paper impresses one with the need of beneficiation, in many cases. Processes of beneficiation will come into their own as our richer ores become exhausted. Many efforts at improvement have been commercial failures, due to prematurity. Thomas A. Edison, with characteristic foresight, attempted concentration of the low-grade New Jersey magnetites, some 30 years ago. Due to high costs and the discovery of the Mesabi range, his efforts were futile. However, a successful crusher, designed by Mr. Edison, resulted from this attempt.

Agglomeration of the concentrates had not, at that time, been brought to its present efficiency, when sinters and briquettes of excellent physical condition are obtainable. Recent efforts in the beneficiation of the lean magnetites of the East Mesabi (anal. 9) resulted in an excellent sinter (anal. 10), but that operation is also ahead of its time.

Sintered Ores

The magnetites of New York are now prepared with excellent results. as shown by the Harob sinter (anal. 20) and New Bed sinter (anal. 21), It is interesting to note that sintered ore from this locality, in excess of 100,000 tons per year, is now shipped to Pittsburgh indicating one of the means of maintaining our position in the steel industry, when the present Superior ores are further depleted.

The preparation of ores in Sweden and Norway has had much attention and is now carried on successfully in Sweden. The concentrating is done by a wet process with a resultant sludge or "slig." These sludges contain too much water for shipment as such and agglomeration is necessary before shipment. The efforts in Norway at Sydvaranger (anal. 86) and Lofoten (anal. 87) have been commercially unsuccessful. The enrichment of hematite ores by flotation has as yet been ineffective but recent reports indicate an approach to success. The roasting of low-grade siderites must receive greater attention in the future, as well as the process of improving the laterites, to which reference has been made. All these processes are essential to the successful use of the enormous quantity of low-grade ore to which we must turn upon the exhaustion of the ores now being mined.

Transportation

Relative location of ores and markets brings the matter of transportation of foreign ores forcibly to our attention, especially ocean shipping, which in fact is the key to the situation. This factor in regard to Spanish ores and English coals, whereby a great trade was developed has already been mentioned. The movement of approximately 10,000,000 tons of ore

from Lapland is another instance, but here, no great return movement compensates. The Lapland ores are shipped from Lulea and Narvik, the former on the east coast of Norway is closed seven months of the year. The greater movement is through Narvik on the west coast and which, due to the Gulf stream, is open all the year. Swedish ore is transported to Germany by steamer to Rotterdam, where it is transferred to barges of 3500 tons capacity, for shipment up the Rhine. This is a highly specialized movement throughout. The docks at Rotterdam are of the most approved type, being principally designed and built by the American Brown-Hoist organization. The steamers are owned by the Swedish ore interests and are specially designed for the purpose. A fleet totalling 700,000 tons burden is used in this ore trade. Under present conditions Rotterdam also handles more than 1,000,000 tons Wabana ore annually.

A highly specialized system of ore transportation has been devised by the Bethlehem Steel interests; it is made necessary by the relative location of their mines in Cuba and Chile and their works on the Atlantic seaboard. In the Cuba trade, boats of 10,000 tons capacity are used, so built, however, with reference to hatches as to give greatest access to modern ore-loading machinery and thereby, maximum despatch with minimum costs. Because of the short haul the total cost of transportation should closely approach that of the Lapland-Germany movement. The importation of Chilean ores presented graver problems, in that the round trip requires at least 42 days with very little tonnage outbound to South America. The situation was met, however, in Bethlehem's usual courageous way in that boats were built of 20,000 tons capacity and, I believe, one of 24,000 tons. They also are constructed for use under the standard "grabs." To the extent possible, return cargoes of coal are obtained, especially to the Panama Canal, and of fuel oil for their mines and other points. Saddle-bag tanks were built into some of their steamers for the purpose of oil transportation. Naturally, no costs of transportation in this movement are public but it is reasonable to assert that it is the lowest per ton—mile of any iron ore transportation on salt water and must very nearly approach the excellent costs obtained by the transportation of the ores on the Great Lakes, in a highly specialized trade.

The Wabana ore is transferred to Sydney, Nova Scotia, in a lesser amount, but equally as efficiently. This season is shorter than that obtaining in the Superior movement and is carried on in boats under time charter, or in other words, rented for the year. Excellent despatch is made, and a unique feature is that the boats are never completely cleaned of iron ore until the last trip. These methods of transportation hold for most of the ores moved. There is however, a considerable tonnage moved each year under regular charter covering a single trip. This situation obtains in the movement of ore from the ports of Spain and North Africa to England, Germany and America. The business of char-

tering is an interesting one and is done almost without exception in "The Baltic" which is an old London institution and, in addition, is the center of the grain trade. "The Baltic" was originally a coffee house where the Russian tallow merchants met in the morning to discuss trade conditions over their coffee. It is easy to see how the grain trade became a part of this exchange, due to Russian influence, and thereby all chartering eventually found its way into the trade. Lloyds also originated in a coffee house and like "The Baltic," extends back over more than 200 years.

"Charter Party" Provisions

The "Charter Party," which embodies provisions for any contingency that may arise in the transportation of any commodity to any port in the world, should be of interest to anyone familiar only with the problems of Lake ore movement. The provisions of this contract are rigidly enforced but due to the exigencies of the case would, no doubt, be considered lenient by Lake ore shippers, in that despatch is of little moment. The rate of freight is usually in shillings per ton (2240 lb.) from which reductions are made for loading and unloading the vessel. Sundry items of port charges are also deductible, even to a charge of £1 for running the lines. Despatch money is provided on a basis of loading and unloading, generally 1000 tons per day of 24 hr. is exacted so that a 6000-ton boat permits a total of 12 days for the two operations. Any time saved accrues to the ore, any overtime is paid to the boat and usually at the rate of £10 or £15 per day, to the end that under most favorable conditions, a boat of this size might pay $1000 despatch money, in addition to the stevedoring expenses. In other words, a steamer of the ordinary "tramp" type would receive net about 90c. per gross ton for the transportation of iron ore from North African ports to the east Atlantic coast, or a haul of about 4500 miles. Many elements enter into this movement and are disturbing to the extent that all chartering is done by the very reliable ore merchants of London, who are alive to cross winds in the world's trade and whose representatives appear on "The Baltic" when in need of steamers. I have detailed the various methods of ore transportation because of the importance of this business in reference to the present and future ore trade of the world.

Merchandising the Ore

The business end of the foreign ore trade is equally unique and centers in London, where a number of reliable firms carry on the trade. Their usefulness is due to the fact that many of the ores are found in countries in which the English language is not spoken and many of the operations are too small to permit of direct handling by the owners. This business is usually done on a commission of three pence per ton to the agent. This method has been in use for a great many years and still holds for strictly merchant ore. At one time, trading in these ores on the American side

was of great magnitude and several firms, acting as merchants, were engaged in the trade. All of them were successful from a financial standpoint. Conditions have changed so that it is believed that only one strictly merchant firm remains in America. Its operation is typical of the manner in which the ore business is conducted in that the chartering and ore purchases are made through its London correspondents, the former along the lines already mentioned; in the latter the customs of the trade are followed and the ore purchases are in shillings per ton with established scales for variations in quality, which have for their basis the physical and chemical properties of the ores. The custom in the London market is to test the ore as to its physical condition by screen tests, reported as follows: lump, that portion remaining on a 2-in. screen; rubble, that portion passing a 2-in. screen but remaining on a ½-in. screen, and smalls, that portion passing through a ½-in. screen. Little attention has been paid to the 100-mesh material known as "Dead Fines," a test brought about by the introduction of Mesabi ores.

Adjustments for Variations

The experience of the foreign operator and these tests classify the ore in the minds of users of foreign ores and penalties and premiums automatically become effective and are reflected in the base price in shillings. Chemically, the adjustments are more involved but, on the whole, work out closely to the scales operative in Lake ore contracts. Variations in silica and iron content call for adjustment from the shilling price per ton, which calls for an iron content of 50 per cent. in the "sample as drawn" or in what we call "natural condition," together with a silica content of 8 per cent. A deviation of 1 per cent. of iron up or down calls for an adjustment of 6 pence per ton and 1 per cent. of silica either way exacts an adjustment of 1½ pence. However, we have a striking example of how physical condition and sulfur affect ore values abroad. The tables below refer to two Bilbao ores of wide difference but which represent the bulk of the Spanish ore trade with England before the war. For purposes of comparison the essential chemical elements and physical tests are shown, as follows:

	Best Bilbao Spathic "Franco Belga," Natural Condition, Per Cent.	Best Rubio "Anita," Natural Condition, Per Cent.
Iron	55.760	48.68
Phosphorus	0.010	0.023
Sulfur	0.450	0.032
Moisture	1.000	8.78
	Physical Test Per Cent	Physical Test, Per Cent.
Lump	30	23
Rubble	30	35
Smalls	40	42

These ores were sold at the same price in shillings per ton f.o.b. Bilbao in spite of their wide divergence in chemical properties. The Spathic is a

calcined ore carrying practically 8 per cent. more iron and 13 points less of phosphorus, in a place where phosphorus counts, but on account of higher sulfur and inferior physical conditions, sells at the same price as the Rubio. These Rubio ores are fully equal to the best "Old Range" American ores obtainable, in addition to the advantages already shown. The sales of Rubio ores were made "tele kel," in other words at shillings per ton, as the ore might run when delivered. This condition compelled the London agent to keep a representative at the Rubio mines at all times, in order that the run of the ore might be known. The many details as indicated by the various regulations in this merchant trade, make plain the usefulness of the London agent.

It is apparent to all that agents or merchants are not required in this country for foreign ores imported from American-owned mines. Many of the larger mines of foreign ownership arrange for representation on this side through agents, on a salary or commission basis. In all cases the ore is offered and sold here on an iron content as found in the ore when delivered, and at a price in cents per unit of iron in the ore in its natural condition. These chemical analyses are made by American chemists, named in the contract. The sampling of these cargoes is the crux of the matter. A knowledge of these "run of the ores" is essential to success in the matter of sampling.

Import Statistics

Statistics of imports of ore are interesting in that the imports for the 40 years, 1882 to 1928 inclusive, totaled 54,674,948 tons, which, closely approximates the average yearly production of 53,733,487 tons from the Lake Superior mines alone. In no single year during this period have imports exceeded 3,000,000 tons and the average annual imports over the last five years aggregated 2,768,430 tons per year, of which two-thirds or 1,711,690 tons came in from American-owned foreign mines and 661,621 tons represented the yearly merchant ore trade for the same period, or approximately 1 per cent. of the total domestic production of iron ore. This small tonnage would seem to indicate that much had been said about nothing, but our real interest in this matter of the exhaustion of the American ore is the substitution of foreign ores in its place. When this condition arises a great increase in the imports of iron ores may be expected and from the data herewith submitted definite conclusions may be drawn.

In conclusion, we are in a position to say that the world's supply of ore seems without limit and we may add, that even to a greater extent, the same condition holds in the United States. I have already cited authorities on the entire known reserves, to which we should add the 20,000,000,000 tons reported by Mr. Perin, which alone added a century's supply to the world's needs, at our present rate of consumption. During

the last three years this has averaged 155,750,000 tons and it is confidently expected that the figure for 1928 will be in excess of 175,000,000 tons; we have produced 79,503,000 tons of pig iron for the three-year average. This places expected pig iron production for this year at approximately 90,000,000 tons. It is interesting to note that the average yield of ores is about 50 per cent. of pig iron. It is indeed difficult to predict the life of these ore reserves based upon any data we now have, either our records of consumption or any conclusions we may draw from the increase shown in annual consumption. This consumption naturally is a progression, whether arithmetical or geometrical, we are not in a position to state, since the elements entering into the problem are too many and too variable to admit of use as a means of determining the end of our reserves. Increase in population is supposed to be the governing factor but it is affected by inventions which may curtail the use of iron in certain industries and increase it in others.

War is another cross-current, with its resultant disorganization. In a Cyrus Fogg Brackett lecture at Princeton University in 1924, Charles P. Perin stated that the actual reserves would be exhausted by the year 2025 and that the potential reserves would be gone within 200 years thereafter, or about 2225. This statement was based on the revised world estimates published in *Iron Age* for July 27, 1922, but inasmuch as all Asia was given 3,267,000 tons in this 1922 estimate and we know of 20,000,000,000 tons in India alone, together with unmeasured tonnages in Africa as against a paltry 400,000,000 tons then estimated to be there, I feel that the year 2225 is much too early for the exhaustion of the world's supply of iron ore. Eventual exhaustion will depend entirely upon the development of beneficiation and transportation. In the former case ores not now workable will come into production, replacing our better ores which will have been depleted. The mechanics of the problem will right themselves, in larger boats and more economical operations. It will be necessary to have return cargoes to the far distant ore mines, in order that the entire trip may be profitable, based upon a reasonable freight for the ore. Undoubtedly, all these conditions will eventually be met.

Domestic Reserves

To a lesser degree these same general statements may be applied to our own conditions in the United States. We hear various estimates that the Lake Superior ores will be exhausted in 30 to 50 years. This may apply to the 1,500,000,000 tons now said to exist in these regions. Even with an average mine production of 51,219,769 tons over the last five years we can have no fear that at the end of the 30-year period our vast industry will cease, not with 72,000,000,000 tons of iron-bearing material in reserve, nor will this transition be sharp and clearly defined but will

occur as it has in the past 40 years, as reflected in a gradual reduction in the yield of iron in the ores as shipped.

Fifty years ago the standard ores yielded 60 per cent. and better and ores of 40 per cent. iron and 40 per cent. silica were introduced to give proper slag volume. The acquisition of the ore mines by the larger corporations and the cooperation of the Lake shippers changed all this, so that the siliceous ores became obsolete and any figuring of mixtures became unnecessary, with the result that ore of uniform but decreasing iron content is shipped to the furnaces each year. This condition has been met by the furnace managers through improvements in design and operation, whereby we have better practice with ores carrying 20 per cent. less of iron than with the richer ores of 40 to 50 years ago. Similar improvements will solve the problem in the future, with the help of beneficiation, so that the iron and steel industry will continue to function in its present territory, within a triangle of which Buffalo, Pittsburgh and Chicago are the determining points. It will be held there by the coal reserves and an advantageous market condition. We may of course expect great development upon the Atlantic seaboard.

At Birmingham, a corresponding increase in production will obtain. When necessary the ores of Tennessee will yield to beneficiation and become available. No iron center is better adapted to the use of foreign ores, through the port of Mobile, than the Birmingham district. The change to foreign ores from Cuba and Brazil will likewise be a gradual transition, based upon world conditions. The same will apply to the northern sea coast and will be in a segment of a circle having Baltimore as its center but with an ever-lengthening radius, due to changes brought about by the ever-changing ratio between the cost of domestic and foreign ores. The United States will therefore continue to be a world factor in the steel industry, but will be in strong competition with that other great producing area, England, France and Germany. England will continue to use her own low-grade siderites and carbonates but in increasing tonnages, together with imported ore from Africa and Spain. France can depend on her own Minette and Germany largely on purchased ore, Minette from France and Luxemburg, magnetite from Sweden and miscellaneous ores from North Africa, Spain and Newfoundland.

We may expect that these two centers will dominate the world. Well-established steel operations will exist in other countries, as a matter of national pride, but none of them can hope to compete in the broadest sense, for they lack one or the other of the conditions required to meet the situation, for it is certain that fuel, ore, and a market are essential to the dominance in this industry.

DISCUSSION

T. T. READ, New York, N. Y.—Mr. Hart has been good enough to mention the brief article on the iron ore resources of China which I prepared for *Iron Ore Resources of the World*, published by the International Geological Congress in 1910. At that time practically no precise information on probable iron ore resources was available and in summarizing what data were available about all I was able to contribute was the observation that although in the case of other metals the best place to look for deposits is in regions where the Chinese have been working them, this is not true of iron ore since the Chinese worked only where ore and fuel were in close proximity, while under modern conditions this combination is not necessary. The relatively small iron-producing industry that has so far developed in China has been in regions where there was no important native industry, while Shansi, the scene of the best known and most extensive native industry, has not been, and probably cannot be, developed on a modern scale.

Since 1910 much exploratory work has been done and is admirably summarized in Tegengren's report, to which reference has been made. My own belief is that this report is pessimistic rather than optimistic in its viewpoint, which is perhaps a natural reaction to the many overexaggerated statements previously made. And it is quite true that even if valuable deposits should be found somewhere in the large areas of Western China that are yet almost unexplored, they would be so remote from markets and face such difficult transportation conditions as to remove them from the sphere of practical consideration for a long time to come. The general situation is that the probable iron ore resources of China are below rather than above probable domestic requirements and that country is likely to remain an importer rather than an exporter of iron and steel.

A. H. HOBLEY, Washington, D. C.—Mr. Hart used the words, "national pride." It might be suggested that certain developments have also often been given consideration because of matters of national defense. Probably, everyone here is more concerned with the use of iron and steel in peace time than in war time, but it is interesting to remember that the possession of iron and steel has been the possible cause of war; also that the location of iron ore deposits might easily affect military operations. For instance, it has been shown that a large percentage of American iron ore lies close to the Canadian border. If we were involved in any military affair that included Canada the United States would therefore have to be protected against the loss of those deposits. Of course, we do not overlook the fact that other iron ore deposits are available, but the output of these other deposits is so small compared with that of the Lake Superior district that a war would undoubtedly be over before their operations could be extended sufficiently to come anywhere near meeting combined military and commercial needs.

F. F. Foss, Wheeling, W. Va.—The iron ore deposits of Russia are situated at many points in this extensive country. From the western boundary to the border of the Pacific Ocean iron ores of different kinds can be found. The most important reserves are in four main regions which I will describe later. Comparatively minor deposits are scattered all over the country and these will also be enumerated. Besides iron ores, Russia has extensive deposits of manganese ore, consisting of two very important and some minor deposits.

The deposit of iron ore which has supplied, up to the present time, the largest amount of ore to the southern iron-producing centers is "Krivoi Rog" ("Curved Horn") in the State of Ekaterinoslav, South Russia. It consists of high-grade hematites occurring in metamorphic schists. These ores contain from 50 to 65 per cent. metallic iron, are low in phosphorus, with 2 to 11 per cent. silica, 0.7 to 3.5 per

cent. alumina, traces of sulfur, less than 1 per cent. of lime and magnesia, and from 0.02 to 0.08 per cent. manganese. Actual reserves are calculated at about 230,000,000 tons. Potential reserves are estimated at about 400,000,000 tons, if 175,000,000 tons of iron quarzites of 43 per cent. iron content are considered. The authority for these calculations is Prof. E. N. Fuchs.

Close to these deposits are the manganese deposits of Nikopol which are estimated at about 75,000,000 tons. The manganese content of the ore before washing is 35 per cent. The first quality ore contains from 46 to 52 per cent. manganese; the second from 40 to 45 per cent.

The second region of iron ore deposits in South Russia is on the Kertch Peninsula, in the Crimea. Actual proven reserves total 450,000,000 tons, and probable and possible reserves are estimated at from 1,500,000,000 to 2,000,000,000 tons. Kertch ores are of brown iron stone containing from 35 to 42 per cent. iron with 1½ to 6 per cent. manganese; phosphorus, about 1 per cent.; sulfur, 0.2 per cent.; arsenic, 0.08 per cent.; silica, 15 per cent.; alumina, 5 to 6 per cent., and moisture, 15 to 20 per cent. Physically this ore is very fine and only 25 per cent. is delivered in lump form, the rest being in a rather fine sandy condition. (Authorities: Professors Bogdanowich and Luchiczky.)

The third region of iron ore deposits is in the Ural Mountains, and may be roughly divided into six districts:

1. Nadezhdinsky district which has mines of red hematite, magnetite and brown ore and contains about 8,000,000 tons. (Authority: Professor Boldirev.)

2. Tagil district where the ores are mostly magnetite and martite (pseudomorphous magnetite with properties of hematite) with actual deposits 38,000,000 tons. Many authorities have expressed opinions on this district and their estimates differ widely. Some figure the potential reserves as high as 130,000,000 tons.

3. Alapayevsky district has 37,000,000 tons of actual and 390,000,000 tons of potential reserves. Ores are of a brown ore type with an average of 38 to 42 per cent. iron.

4. Bakal district contains high quality siderites which in the upper zones have been changed into brown ore. Estimates of the reserves of this district run as high as 45,000,000 tons. Prof. A. Zavariczky and other authorities give figures as high as 74,000,000 tons.

5. Komarov district also has high quality brown ore; potential reserves, 50,000,000 tons.

6. Gora Magnitnaya deposits consist of magnetites transformed in the upper zones into martites and contain 275,000,000 tons. (Authority: Prof. A. Zavariczky.)

The fourth region of iron ore deposits of some importance is in the Altai Mountains in Siberia. There is a group of iron ore deposits, the most prominent being Telbes (near Kouznetzk City, State of Tomsk) which contains as much as 5,000,0000 tons of different ores. The largest part of this ore runs 60 per cent. magnetites; siderites and limonites are also present. Estimates on the total deposits of this region run as high as 20,000,000 tons. (Authority: Professors P. P. Goudkov and A. A. Sniatkov.)

Among regions of lesser importance, which have iron ore deposits, the following may be mentioned:

Lipetzk and Tula districts with limonites of 45 to 50 per cent. iron content. These deposits are scattered over a very wide area and are estimated on different bases by several authorities. Actual, commercial reserves, which can be mined at the present level of prices on iron products are calculated to be close to 50,000,000 tons. Probable deposits may be estimated at as much as 500,000,000 tons and even more. (Authority: A. K. Meister.)

The same kind of limonites and to a great extent bog ores are located in the State of Olonez. Bog ore deposits of Povenez and Ukchosero of 30 per cent. iron content are calculated at approximately 80,000,000 tons. There are also magnetite iron ores in the Olonez region which are roughly estimated at 10,000,000 tons.

The limonites of 30 to 50 per cent. iron of Vyatka region are estimated at about 40,000,000, tons.

Southern Caucasus has deposits of magnetite ores, the extent of which has been variously estimated. In any event these deposits are of commercial importance.

The largest manganese ore reserves of Russia are located in Georgia, in Southern Caucasus, close to the seaport Poti. These well known deposits are in the region of Tchiatouri and contain from 50,000,000 to 100,000,000 tons of manganese ore, which after washing, gives from 48 to 52 per cent. manganese.

Minor deposits of iron ore in Siberia are located in the following regions:

Irkoutsky region has deposits of magnetites of 40 to 55 per cent. iron and contains about 3,000,000 tons.

Minoussinsky region has magnetites of 65 per cent. iron content, siderites and limonites, and is estimated to contain about 5,000,000 tons.

On the Pacific coast there is a deposit of magnetite close to the Saint-Olga Bay. It is estimated at as high as 6,000,000 tons.

The above figures show that actual resources in iron ores of Russia may be estimated at 1,150,000,000 tons with potential reserves as high as 2,750,000,000 tons.

G. B. WATERHOUSE, Cambridge, Mass.—I have spent the summer in Cape Breton, so I have naturally heard a good deal and thought a lot about the Wabana ore. Eckel's estimate of 6,000,000,000 tons, is much too low, I am sure. The authority on the Wabana ore is Dr. Hayes, who is the head of the Geology Department at Rutgers University. He is at present in Newfoundland going over the mining operations from the geological standpoint. I feel sure that the estimate of 10,000,000,000 tons for the Wabana deposits is much nearer the mark than that of Eckel. So our total of 150,000,000,000 tons for the world constantly expands. I have been in close contact with Brazil. I spent a great deal of time recently with the son of the president. He operates the only iron foundry of any size in that country, melting about 60 tons a day of iron in his foundry. He tells me that the resources of ore are really yet unknown, that in the great state of Minas Geraes, which is the one which Mr. Hart undoubtedly had in mind, there are wonderful supplies of ore that have not by any means been charted.

The recently established Farquhar concession may bring to our country large quantities of high-grade hematite from Brazil in the near future.

Mr. Hart did not mention our Pacific Coast deposits. I know of a deposit fairly close to the Columbia River, very much of the order of the laterite deposits we have heard of. It has been proved very thoroughly with diamond drill cores, and the estimate is about 10,000,000 tons, not by any means a large deposit, but quite appreciable, and it may be of considerable importance to the Pacific Coast industries when they begin to need iron ores.

Mr. Hart did not mention South Africa, which is known to have extensive deposits of red hematite. Under government auspices much attention is being given to the founding of an iron and steel industry there, based on is own iron ores.

The laterites of the north coast of Cuba may easily be of great importance. I have been paying some attention to a deposit known as the Moa Bay deposit of the same general type, and very closely situated to the Bethlehem Mayari deposits, and I am sure we know little about the iron ore resources of the West Indies. Friends of mine are interested in developing hematite deposits in Porto Rico, of which we know nothing as to extent and amount.

Iron-ore Sinter

By G. M. Schwartz,* Minneapolis, Minn.

(Cleveland Meeting, September, 1929)

There has been considerable controversy regarding the structure and mineral constituents produced when iron ore is sintered. This investigation was undertaken in order to establish the fundamental reactions that take place in the sintering process by determining the nature of the resulting minerals. The writer's immediate interest in the subject arose mainly from the request of E. W. Davis for information based on a microscopic study of sinter submitted by him in May, 1926.

In the author's preliminary work, samples of iron-ore sinter were secured from the Minnesota School of Mines Experiment Station and from commercial plants. These were polished by the usual methods for polishing opaque ores. In order to study these surfaces satisfactorily, it is necessary to magnify them rather highly, a range from 100 to 1000 dia. being used. For the higher magnifications oil-immersion lenses and an intense source of light are necessary.

After the preliminary study had shown the problems involved, a series of small samples were sintered under carefully controlled conditions and with analyzed materials. Variations in the relative amounts of ore, coal and water were made in order to study the effect of each constituent.

The attempt has been to arrive at a clearer understanding of the sintering process and the reactions involved without reference to any preconceived notion as to sinter. It is clear that the study of polished surfaces has yielded results not possible with thin sections alone. The thin sections made in this work were found unsatisfactory at magnification greater than 75, whereas magnifications of 1000 were easily studied with reflected light on carefully polished surfaces. A rather complete statement of observed facts is made so that the reader may form his own conclusions. The writer's interpretations are suggested.

It is to be hoped that a more complete understanding of the structure and composition of iron sinter, as well as the changes which go on during

* Department of Geology and Mineralogy, University of Minnesota.

sintering will be beneficial to the process, which is becoming more and more generally used as lower grade ores are mined. Needless to say there remains much to be done, especially in studying sinter from commercial plants produced under varying conditions and with various ores. Our studies seem to indicate that the iron-ore sinter is much the same regardless of the type of ore, but this probably would not hold true if the amount and nature of the gangue material varied widely.

The Sintering Process

The sintering process, as distinct from the nodulizing and briquetting of very fine ores or concentrates was the outcome of a series of experiments carried out by A. S. Dwight and R. L. Lloyd in the plant of the Cananea Consolidated Copper Co. At about the same time, John E. Greenawalt was developing a similar process, so that we now have two sintering processes which produce material of about the same structure.

The Dwight-Lloyd process was briefly described by Dwight in an article published in 1908.[1] The process as first evolved was not satisfactory for iron ores. Further experimentation resulted in an application for a patent on June 17, 1911, but this was not issued until Jan. 27, 1918. The first plant treating iron ore was started in September, 1911, at the E. and G. Brooke Iron Co. works at Birdsboro, Pennsylvania.

Usually, a thin layer of fine ore together with a small percentage of coal or other fuel moistened with water is spread on the sintering machine. The fuel in the surface layer of the charge is ignited and the air is drawn down through the bed so that combustion, initiated at the surface, is carried progressively downward through the bed in a narrow high-temperature zone. When the high-temperature zone has progressed to the bottom of the bed the sinter cake is discharged.

The burning of the fuel develops sufficient heat to effect fusion of most of the mineral particles and causes partial reduction and recombination of the iron oxide, so that the mass crystallizes into new forms. The period of intense heat for any part of the charge is extremely brief, on account of the cold air currents. The air is also responsible for the development of the porosity characteristic of sinter. Only a few minutes is required to sinter a 4-in. bed, and any given particle in that bed is subjected to the maximum heat for a short time only.

The sintered product is ideal material for charging to a blast furnace. Physically it is a cellular, porous, but strong lump of iron oxides presenting an enormous surface to the action of the reducing gases.

---

[1] A. S. Dwight: The Dwight-Lloyd Sintering Process. *Eng. & Min. Jnl.* (1908) 85, 649.

For commercial plants a continuous type of machine is used, but for experimental purposes small pans may be utilized. For the series of experiments described in this paper a small cup about 4 in. dia. was used and very satisfactory results were obtained.

Previous Work on Iron-bearing Materials

Comparatively little has been published on the microstructures of iron-ore sinter or on any phase of the process. Some studies have been made with thin sections but a preliminary paper by the writer[2] is the only published material on polished surfaces of iron-ore sinter.

In 1911 Gayley[3] published a short paper dealing especially with the process as applied to flue dust. The cellular nature of the product was emphasized in relation to its reaction in the blast furnace.

A valuable contribution to the subject was made by Klugh[4] in 1912, which caused much discussion at the Institute meeting at which it was presented. The nature of the action in sintering was analyzed and the product of the Dwight-Lloyd process compared with sinter from other processes. An absence of iron silicate in Dwight-Lloyd sinter was claimed and the iron was stated to be partly in the metallic state and partly as ferrous and ferric oxide. The sinter was stated to be an agglomeration of the material treated, being bonded particles of original size. Some of these points will be discussed later in the light of the data presented in this paper.

Vogel[5] presented a paper at the same time dealing mainly with flue dust. Several processes were described. In discussing Vogel's paper Klugh[6] claimed that the Dwight-Lloyd sinter is a product of incipient fusion and that the process represents the least degree of fusion that effectively binds the material.

The importance of the degree of fusion was emphasized in a still later paper by Klugh.[7] The conclusions are stated as follows:

1. The permeability of the cell of a sintered product varies inversely as the degree of fusion to which it has been subjected.

---

[2] G. M. Schwartz: Magnetite Crystals in Sinters. *Eng. & Min. Jnl.* (1927) **124,** 453.

[3] J. Gayley: The Sintering of Fine Iron-bearing Materials. *Trans.*, A. I. M. E. (1911) **42,** 180.

[4] B. G. Klugh: The Sintering of Fine Iron-bearing Materials by the Dwight-Lloyd Process. *Trans.*, A. I. M. E. (1912) **43,** 364.

[5] F. A. Vogel: Sintering and Briquetting of Flue Dust: *Trans.* A. I. M. E. (1912) **43,** 381.

[6] B. G. Klugh: Discussion. *Trans.*, A. I. M. E. (1912) **43,** 739.

[7] B. G. Klugh: The Microstructure of Sintered Iron-bearing Minerals. *Trans.*, A. I. M. E. (1913) **45,** 330.

2. In a product of complete fusion, the silica present combines with its equivalent of iron oxide to form a perfect glass, which, from its greater fluidity, envelops and seals up the remaining iron oxide from the action of gases.

3. Conversely of the foregoing conclusion, in the product of the lowest degree of fusion, the iron oxide and slag-forming materials as a unit are bonded together by incipient fusion, leaving the predominant iron oxide free and vulnerable to the action of gases in the highest degree attainable in solid products.

4. The above salient facts show the Dwight-Lloyd products, when properly made, to possess those properties which distinguish them from the products of other sintering processes or agglomeration methods, by freedom from those constituents to which scouring action in the blast furnace is attributed.

In discussion, Johnson[8] stressed the importance of the cellular structure in relation to fuel economy.

Experimental Sinter

In our investigation, the problem of the structure and minerals of iron-ore sinter was first attacked by studying microscopically samples of

Table 1.—*Sinter Not Specially Made for This Investigation*

Commercial sinter
- Tennessee Copper Co.
- Ducktown Chemical and Iron Co.
- East Mesabi Co. (several samples)
- Reading Iron Co.
- Blast-furnace flue dust, American Ore Reclamation Co.
- 1/3 filter cake and 2/3 flue dust, American Ore Reclamation Co.
- Cornwall concentrate, Bethlehem Steel Co.
- Magnetite nodule, Benson mine
- Briquet, Moose Mountain plant

Experimental sinters, Minnesota Mines Experiment Station
- Shenango pit, Mesabi range
- Pearson mine, Mesabi range
- Bennett mine, Mesabi range, 8 per cent. coal
- Bennett mine, Mesabi range, 10 per cent. coal
- Mahoning mine, Mesabi range
- Pilot Knob, Missouri
- Namekan magnetite concentrate, Minnesota
- Kennedy mine, Cuyuna range
- Mayville, Wisconsin, ore
- Red ore roasted and concentrated magnetically, Birmingham, Alabama
- Titaniferous magnetite concentrate, Minnesota. (Two samples from different ores)
- Flue-dust sinter, American Sintering Co.
- Pyrrhotite ore, Atikokan, Canada
- Manganese concentrate, Minnesota
- Steel shavings sintered
- Chemically precipitated iron oxide
- Chemically precipitated iron oxide plus 25 per cent. SiO_2
- Unlabeled sinter, T. M. Broderick's collection

[8] J. E. Johnson, Jr.: *Trans.*, A. I. M. E. (1913) **47**, 351.

all of the available sinter, some from commercial plants and many from ore-dressing experiments made at the Minnesota School of Mines Experiment Station. In some cases more or less complete analyses of the unsintered ore were available, thus giving a valuable check on the microscopic work. Table 1 gives a list of samples of this type.

After examination of the available sinter a series of experiments was outlined with the idea not only of furnishing for microscopic study sinter which had been produced under varying conditions, but also of determining the effect of varying the relative amounts of ore, fuel and water present in the material to be sintered. For this purpose it was advisable to know the exact composition of the sinter, consequently both ore and coal were analyzed. The ore used was magnetite concentrate from the East Mesabi range. Pocahontas coal was utilized in all cases. A large batch was crushed and analyzed and reserved for this purpose. The analyses of ore and coal are given in Table 2 and data on experimental sinter made for this investigation are listed in Table 3.

TABLE 2.—*Analyses of Ore and Coal*

Mesabi Magnetite Concentrate	Per Cent.	Coal	Per Cent.
Fe	60.12	H_2O	0.70
SiO_2	12.28	Volatile matter	26.06
Al_2O_3	0.29	Fixed C	66.44
CaO	0.69	Ash	7.50
MgO	0.94	SiO_2	3.46
		Al_2O_3	1.80
		CaO	0.17
		MgO	0.07

It was found that the coal content could be varied for this particular ore from about 4 to 11 per cent. of the dry charge. Within these limits this variation in fuel produced surprisingly little difference except in the toughness, which varied as shown in Table 3.

A rather high water content was found necessary for the ore and machine used. Greater than 16 per cent. could not be used because the mixture became a mud (series D, Table 3). Commercial ores are sintered with as little as 5 per cent. water. It was found that the higher water resulted in a more friable sinter, which showed under the microscope a lesser degree of crystallization. The lower water content seems most desirable in commercial operations. The maximum and minimum percentages of fuel and water vary greatly with the type of ore.

MICROSCOPIC STUDY OF SINTER

Polishing Methods

The polishing of iron-ore sinter presented no unusual difficulties although the exceedingly rough form necessitates considerable care when

working on the cloth-covered wheels. The system used in these studies is the same as that for polishing ores for microscopic study. The methods are described in several places.[9]

Fragments of fairly coherent sinter are polished without embedding in any supporting material. The most convenient size is a lump about 1½ in. dia. This is ground on a rotating plate, using a paste of 46 or 120 alundum. The flat surface may likewise be obtained by grinding by hand on a coarse carborundum or alundum stone. An emery wheel may be used, but the high speed often breaks the specimen and gives a less satisfactory surface. The next step is to grind the flat surface to a more perfect plane by rubbing on a plate glass with alundum 5f, followed on another plate by alundum 60f. About one minute on each plate is usually sufficient but in some cases more time may be spent to advantage. Up to this point the process may be considered as grinding. It is then necessary to polish the ground surface to produce a mirrorlike polish. For polishing it is necessary to have rapidly rotating disks which can be mounted with cloth ordinarily held on by a band on the disk wheels. The best grade of sheeting has been found most satisfactory for this purpose. At least two surfaces, or both sides of a disk, are necessary. On the first surface alundum 60f suspended in water is applied with a small paint brush; on the second, fine chromic oxide suspended in water is used in the same manner. The ground surface is carefully beveled on all sides to prevent tearing the cloth and the flat surface is applied to the wheel and given a rotating motion to polish the specimen evenly. Considerable pressure must be used with hard materials such as sinter. It is necessary to wash the specimen between each of the steps outlined, to prevent contamination of the successive abrasives, which would scratch rather than polish the specimen. In polishing soft ores the final polish is given on an additional cloth wheel, but this is entirely unnecessary for iron-ore sinter because of the hardness of the minerals.

For the more friable sinter some support is necessary. It was found satisfactory to embed small fragments of sinter in sealing wax by placing them in a pasteboard mold and pouring in the molten wax. In some cases a larger fragment was impregnated by immersing it in the molten sealing wax and heating gently for a few minutes.

Iron-ore sinter takes a brilliant polish, and magnifications up to 1000 dia. were used without much difficulty. A satisfactory method of polishing could be easily adapted from equipment available at most

[9] J. Murdock: Microscopical Determination of the Opaque Minerals. New York, 1916. John Wiley & Sons.

W. M. Davy and C. M. Farnham: Microscopic Examination of the Ore Minerals. New York, 1920. McGraw-Hill Book Co.

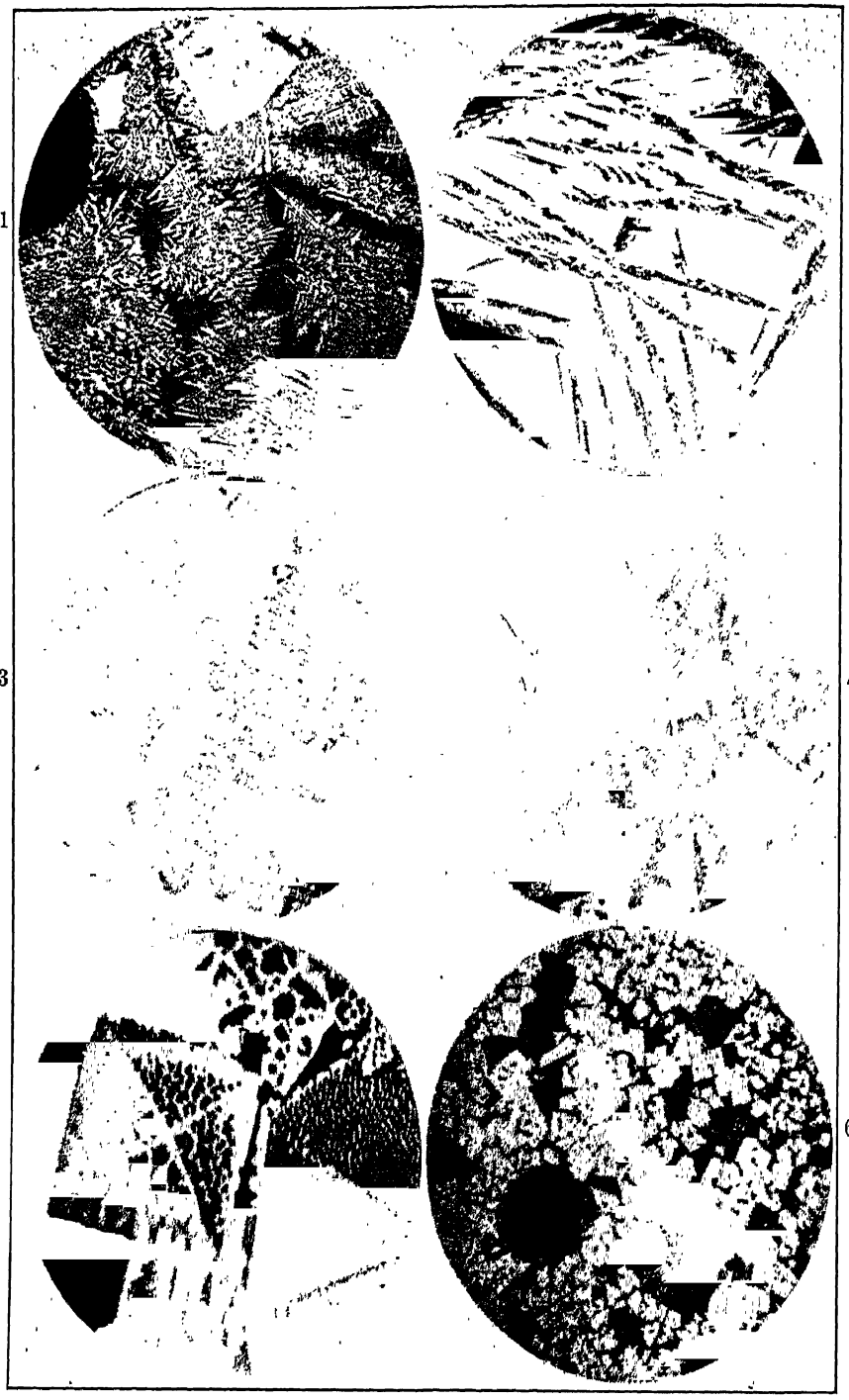
M. N. Short: The Preparation of Polished Sections of Ores. *Econ. Geol.* (1926) **21**, 648.

G. M. Schwartz: Discussion. *Econ. Geol.* (1927) **22**, 193.

metallurgical plants. Satisfactory examination requires a microscope with an intense source of light like that furnished by an arc lamp.

TABLE 3.—*Experimental Sinter Made for This Investigation*

No.	Ore, Per Cent.	SiO_2 in Ore, Per Cent.	Coal, Per Cent.	H_2O Added, Per Cent.	Suction Pressure, Millimeters	Time, Minutes	Remarks
			SERIES A				
1	90		10	10	15	15	Poor
2	91		9	10	15	15	Fair
3	92		8	10	15	15	Good
4	93		7	10	15	15	Good
5	94		6	10	15	15	Good
6	95		5	10	15	15	Very good
7	96		4	10	15	15	Good
			SERIES B				
1	89		11	11	15	20	Very fragile
2	90		10	11	15	20	Fragile
3	91		9	11	15	20	Fragile
4	93		7	11	15	20	Good
5	94		6	11	15	15	Good
6	95		5	11	15	15	Good
7	96		4	11	15	15	Fair
			SERIES C				
1	90		10	12	15	25	Powder
2	91		9	12	15	45	Very fragile
3	92		8	12	15	20	Fragile
4	93		7	12	15	10	Good
5	94		6	12	15	10	Good
6	95		5	12	15	10	Good
7	96		4	12	15	10	Good
			SERIES D				
1	90		10	13	15	30	Poor
2	90		10	14	15	30	Fair
3	90		10	15	15	30	Fragile, poor
4	90		10	16	Made mud—not sintered		
			SERIES E				
1	92	15	8	12	15	20	Fair
2	92	20	8	12	15	15	Good
3	92	25	8	12	15	15	Good, not very tough
4	92	30	8	12	15	25	Fair, brittle
5	92	35	8	12	20	20	Good, but brittle
6	92	40	8	12	20	20	Fair, brittle
7	90	45	10	12	15	25	Good, but brittle
8	90	50	10	12	15	20	Brittle



FIGS. 1–6.—CAPTIONS ON OPPOSITE PAGE.

Opaque Minerals

In all the sinter examined magnetite predominates over all other constituents. Hematite is common though not usually abundant. In sinter from titaniferous ores bladelike forms of ilmenite are common (Fig. 2). No other opaque constituents were recognized, although metallic iron has been reported[10] in sinter and ferrous oxide has been suggested as a possibility.

In certain intergrowths of iron oxide in iron silicate to be described later it is difficult to identify the opaque constituent, since magnetite, ferromagnetic ferric oxide[11] and ferrous oxide[12] all appear much the same on polished surfaces. The writer was unable to see even the slightest difference between the iron oxide of the intergrowth and the adjacent crystals of magnetite and therefore called it all magnetite. It seems unlikely that metallic iron is an important constituent of a normal sinter; if it were, it would have been recognized in some of the many sinters studied. It was found in a flue-dust nodule.

Magnetite

Magnetite (Fe_3O_4 or $FeO.Fe_2O_3$) normally forms from 90 to 99 per cent. of the metallic minerals in the sinter. The usual sinter is highly magnetic and under the microscope the isometric crystal form of the magnetite is evident (see photomicrographs). The material corresponds to the natural mineral in all respects that could be tested and there is no need for a special term to designate it.

[10] B. G. Klugh: The Sintering of Iron-bearing Materials by the Dwight-Lloyd Process. *Trans.*, A. I. M. E. (1912) **43**, 364.

[11] R. B. Sosman and E. Posnjak: Ferromagnetic Ferric Oxide, Artificial and Natural. *Jnl.* Wash. Acad. Sci. (1925) **15**, 329.

[12] R. W. G. Wyckoff and E. D. Crittenden: The Preparation and Crystal Structure of Ferrous Oxide: *Jnl.* Amer. Chem. Soc. (1925) **47**, 2876.

FIG. 1.—AREA CONTAINING NUMEROUS DENDRITES OF MAGNETITE IN GANGUE. COMMERCIAL SINTER, MESABI IRON CO., MINNESOTA. ×270.

Areas such as this are common in most iron-ore sinter.

FIG. 2.—NUMEROUS BLADES, PRESUMABLY ILMENITE, IN SILICATE. EXPERIMENTAL SINTER OF TITANIFEROUS MAGNETITE ORE, MINNESOTA. ×100.

FIG. 3.—UNUSUALLY PERFECT DENDRITES AND SKELETON CRYSTALS OF MAGNETITE. SINTERED CONCENTRATE FROM SHENANGO PIT, MESABI RANGE, MINNESOTA. ×100.

These develop only where silicate is abundant in sintering relative to magnetite. The short time involved in sintering as well as lack of abundant iron tends to retain such structures. Note well-developed sheaf structures of fayalite (*F*).

FIG. 4.—NUMEROUS CRYSTALS OF MAGNETITE ARE OUTLINED BUT NONE ARE QUITE COMPLETE. SAME SINTER AS FIG. 3. ×200.

Figs. 3 and 4 show clearly how dendrites grow cross arms, then connect by diagonals to form square outline. Crystals are probably octahedrons.

FIG. 5.—COMPLETELY OUTLINED SKELETON CRYSTAL OF MAGNETITE. EXPERIMENTAL SINTER, 75 PER CENT. PURE Fe_2O_3 AND 25 PER CENT. SiO_2. ×650.

Presumably a cross-section of an octahedron.

FIG. 6.—SKELETON AND COMPLETE CRYSTALS OF MAGNETITE IN SILICATE. SAME SINTER AS FIG. 5. ×200.

Note pores in silicate. Typical field of iron-ore sinter.

As would be expected from the fast cooling of the sinter, the magnetite occurs as minute grains, dendrites, skeleton crystals, and crystals (see especially Figs. 1 to 8). In fact, the perfection of crystallization of the magnetite would not be suspected unless polished surfaces were examined at magnifications of 100 dia. or higher.

The usual form of the magnetite in sinter is as somewhat imperfect crystals such as those in Fig. 6. Magnetite is recognized among natural minerals as having a strong crystallizing power which causes it to assume its external crystal form if conditions are at all favorable. The greater the amount of silicate present, the more perfect the crystal form of magnetite grains in sinter, due to a lack of interference of the magnetite grains with one another during crystallization. Possibly the difference in the melting points has an effect on crystallization. The melting point of pure fayalite (Fe_2SiO_4) is 1335° C. according to the most recent work[13] and that of magnetite[14] is given as 1538° C. If the magnetite crystals interfere during crystallization polyhedral grains result as shown in Fig. 14. Polyhedral grains are abundant when silicate is small in amount or lacking.

A rather characteristic feature of most sinter is the variation in size of the magnetite crystals. Polished surfaces of small specimens often show areas in which the crystals are three or four times as large as in near-by areas.

Where silicate material is abundant it often happens that the amount of iron oxide available is insufficient to form complete crystals in the short time that the sinter is at high temperatures. As a result, various stages of crystal growth are preserved from the initial dendritic stage to practically complete crystals. Some of these stages are shown in Figs. 1 to 5.

Careful study of the areas showing the dendrites and skeleton crystals reveals the probable method of crystal growth, which is similar to the growth described in alloys and slags. The growth presumably started at a small nucleus and proceeded mainly in three directions at right angles (Fig. 3). Only two directions are visible in the two dimensions of the photographs. Growth seemed to proceed more rapidly in one direction than the other, resulting in the elongate dendrites with cross arms shown in Fig. 3. As growth continued there was a tendency for the ends of the crosses to connect and form a square (in cross-section) with the original cross as diagonals of the square (Fig. 4). These square outlines are no doubt the cross-sections of octahedrons, the common crystal form of magnetite. As crystallization proceeded still farther a complete network was formed, as shown in Fig. 6, and eventually complete crystals formed,

[13] C. H. Herty and G. R. Fitterer: The System Ferrous Oxide-silica. *Ind. & Eng. Chem.* (1929) **21**, 51. See also for a summary of previous determinations.

[14] International Critical Tables, **1**, 128.

is shown in Figs. 7 and 8. Exhaustion of available material may check the process at any stage. Presumably if time enough were available at proper temperatures the material in the dendritic and skeletal forms would rearrange itself to form solid crystals. The short time available in the sintering process may obviously inhibit this rearrangement. The presence of innumerable variations of these dendrites and skeletal forms is an exceedingly characteristic feature of most of the sinters studied. They are fully as common in commercial sinter as in the experimental product. They do not, as a rule, make up more than a small percentage of the sinter and are abundant in the larger areas of silicate.

A great deal of work has been done on the manner and causes of growth of crystals. Desch[15] has recently summarized the knowledge of the growth of metallic crystals. Regarding the development of dendrites he says,

> when growth is rapid, it will be seen that the supply to the faces may be insufficient, so that growth is confined to the angles. The more acute these become, the more the effect is intensified, and there is a tendency for the crystals to elongate at each angle, forming an acute star. Such a structure is likely to be unstable, and a slight disturbance will set up new crystal growth. A rapidly advancing point will enter a zone in which the supply is more favorable, and branching will occur . . . The point behaves as a nucleus, with its orientation determined by a parallel series of new growths, building up the dendrite. Secondary and tertiary branches are formed in the same way, and in course of time more solid is added to each of the crystal surfaces thus produced, until the gaps are filled and the crystal has become a homogeneous mass, the structure of which is only revealed on subsequent etching.

Tutton[16] attributes the formation of dendrites to rapidity of crystallization in a labile solution, there being inadequate time for the formation of well developed crystals.

Study of sinter containing silicates under high magnification reveals other relations and forms which suggest further complexities in crystallization. Two types of microscopic intergrowths of iron oxide (magnetite?) and silicate (normally fayalite, Fe_2SiO_4) may be frequently observed. The first has been called a graphic intergrowth or a eutectic structure (Figs. 9 and 10); the second is a crystallographic intergrowth in which the distribution of the magnetite is obviously determined by the crystal structures of the silicate (Figs. 11 to 13).

That the eutectic structure or pattern shown in Figs. 9 and 10 closely resembles that formed in metallic alloys where the eutectic composition is realized may be observed by comparing the figures with those shown by Miss Green in a recent paper.[17] A logical interpretation placed on

[15] C. H. Desch: Growth of Metallic Crystals. *Trans.*, A. I. M. E. (1927) **75**, 526.

[16] A. E. H. Tutton: The Natural History of Crystals. London, 1924.

[17] C. H. Green: Eutectic Patterns in Metallic Alloys. *Trans.*, A. I. M. E. (1925) **71**, 651.

FIGS. 7–12.—CAPTIONS ON OPPOSITE PAGE.

this structure is that with a proper composition and under certain conditions the magnetite and silicate form a eutectic mixture in which both constituents solidify simultaneously. This type of structure is found not only in alloys and sinter but also in igneous rocks and in ores which have formed by vein deposition. Structures of this type in ores are not considered by many students to originate by eutectic deposition. The evidence seems clear that they may form in other ways; for example, by replacement. When found, however, in sinter or in igneous rocks, the structure may logically be considered to represent eutectic deposition. Magnetite has been found by the writer to form such a structure with silicate in the titaniferous magnetite deposits of the Duluth gabbro.

The work on the equilibrium diagram of the system $FeOSiO_2$[18] shows that there is a eutectic between fayalite (Fe_2SiO_4) and FeO. Either there is a similar eutectic between fayalite and magnetite (Fe_3O_4) or the material resembling magnetite in these intergrowths is FeO.

Intergrowths of the second type (Figs. 11 to 13), in which the crystal structure of the silicate controls the form of the magnetite (?), probably originate in another manner. It is well known that many elements or compounds may hold other elements or compounds in the solid state, forming the so-called "solid solutions," or isomorphous mixtures. In some cases this solution is maintained at all temperatures below the melting point. In other cases the dissolved mineral becomes insoluble below certain temperatures and results in the breaking down of the solid solution into two phases. Commonly the one in excess controls and the minor constituent is relegated to certain spaces in the crystal. The titaniferous magnetites present a well-known example from nature in

[18] C. H. Herty and G. R. Fitterer: *Op. cit.*

FIG. 7.—AREA OF MAGNETITE GRAINS AND CRYSTALS HIGHLY MAGNIFIED. COMMERCIAL SINTER, MESABI IRON CO., MINNESOTA. ×600.
Note tendency of silicate (dark) to surround magnetite grains, thus acting as a binder.

FIG. 8.—TITANIFEROUS MAGNETITE SINTER SHOWING PERFECT MAGNETITE CRYSTALS (*M*) WITH DENDRITES OF ILMENITE ($FeTiO_3$) IN SILICATE. MAGNETITE CONCENTRATE FROM DEPOSITS IN DULUTH GABBRO. ×200.

FIG. 9.—S NTER SHOWING MAGNETITE CRYSTALS (*M*) AND MAGNETITE AND SILICATE IN INTERGROWTH SUGGESTING EUTECTIC. EXPERIMENTAL SINTER A4. ×250.
This texture has been referred to in geological literature as a graphic intergrowth.

FIG. 10.—EXPERIMENTAL SINTER E7. ×800.
This area under low magnifications appeared to be silicate. Under the oil-immersion lens it proved to be an intergrowth of iron oxide (light) and silicate (dark). Probably a eutectic of fayalite and Fe_3O_4 or FeO.

FIG. 11.—CRYSTALLOGRAPHIC INTERGROWTH OF MAGNETITE AND SILICATE. MESABI IRON CO., MINNESOTA. ×500.
This structure probably resulted from the breakdown of a solid solution of magnetite in silicate at high temperature. On cooling the magnetite became insoluble and precipitated out. Note the magnetite crystal (*M*).

FIG. 12.—SIMILAR TO FIG. 11, BUT VARYING IN DETAIL. COMMERCIAL SINTER, MESABI IRON CO., MINNESOTA. ×438.
Form of magnetite is due to arrangement along crystallographic directions in silicate. Photo by T. M. Broderick.

which plates, blades, and other forms of ilmenite ($FeTiO_3$) are oriented along the octahedral planes of the magnetite crystal.[19]

Figs. 11 and 12 are examples of this structure in sinter. Nearly all of the iron oxide is distributed as crystallographic intergrowths in silicate. Fig. 13 shows sinter from the East Mesabi plant where the intergrowth acts as a matrix to nearly perfect crystals of magnetite. It is noteworthy that there is no difference in the appearance between magnetite crystals and the intergrown iron oxide, which is therefore considered to be magnetite.

The formation of a crystallographic intergrowth of the type described may be explained as follows: When the material was molten it was doubtless homogeneous; as it cooled excess Fe_3O_4 became insoluble and crystallized out, forming nearly perfect crystals of magnetite. Some of the Fe_3O_4 remained soluble in the molten silicate, which on further cooling solidified as a solid solution of silicate (mainly fayalite, Fe_2SiO_4) and magnetite. As the solid cooled, Fe_3O_4 became insoluble in the silicate and was precipitated out or excluded from the lattice of the silicate. The magnetite could not escape from the fayalite crystals but arranged itself among certain crystallographic planes in the silicate, resulting in the textures shown in Figs. 11 to 14. An explanation of what happens in terms of atoms and the space lattice when the breakdown occurs has recently been given by Desch.[20] This may be applied to the present case. It has also been suggested that this structure may be explained by considering the silicate and magnetite as forming a binary system corresponding to Roozeboom's Type V, in which two limited series of solid solutions are formed, between the limits of which a eutectiferous series of alloys occurs.

It was observed that in areas of very small magnetite crystals, or dendritic forms, the silicate is usually filled with intergrown magnetite. Where magnetite formed good crystals there seems to have been time for much of the magnetite to be excluded from the silicate during cooling. It seems apparent that the great variety of forms and relationships shown by sinter are the result of the rapidity with which the sintering process takes place and the very short time involved in the complete process.

Under certain conditions magnetite apparently does not have an opportunity to crystallize in any of the forms described above but remains as globular grains in a silicate matrix, as shown in Fig. 16. This form was not common in any of the commercial sinter examined, but was rather abundant in certain samples of the experimental sinter listed in Table 3. It was particularly abundant in Nos. 1, 2, 3, 4 of series B, 6 and

[19] See, for example, J. T. Singewald: The Titaniferous Iron Ores of the United States. U. S. Bur. Mines *Bull.* 13 (1913).

[20] C. H. Desch: The Chemical Properties of Crystals. *Jnl.* Inst. of Metals (1928) **39**, 411.

7 of series C, 1 and 3 of series D. We can only speculate as to the cause of this form.

Hematite

The outside of the sinter cake is often rather reddish in color and more friable than the interior. This is due to the presence of considerable amounts of hematite of the soft earthy type. In the ordinary sinter hematite is usually found on microscopic examination in small amounts around the edges of pores and penetrating the magnetite along the octahedral planes, as shown in Figs. 17 and 18. Fig. 17 clearly shows that hematite is a late development, doubtless formed by oxidation while the sinter is cooling and where the air has free access. This development of hematite normally starts along the octahedral planes. This is true of the oxidation of magnetite in nature, as has been noted by Broderick.[21] Gruner[22] also found this to be the case when natural magnetites were artificially oxidized by heating in air. In all satisfactory sinter the amount of hematite is small, perhaps not over 2 or 3 per cent. In some cases, noted particularly in commercial sinter from the Reading Iron Co. plant, the hematite formed shells around the outside of small magnetite crystals (see Fig. 19). This sinter also shows a marvelous development of hematite along the octahedral planes of the magnetite crystals (Fig. 18). At some places the hematite occurred along the octahedral planes in the inside of magnetite grains but the outside of the grain was free from visible hematite. This structure suggests that some hematite may have remained in solution in magnetite and precipitated out on cooling or that possibly it is residual hematite which did not change to magnetite. Too much significance should not be attached to this occurrence, however, since it is rare and is found in a specimen which contains an obviously later generation of hematite.

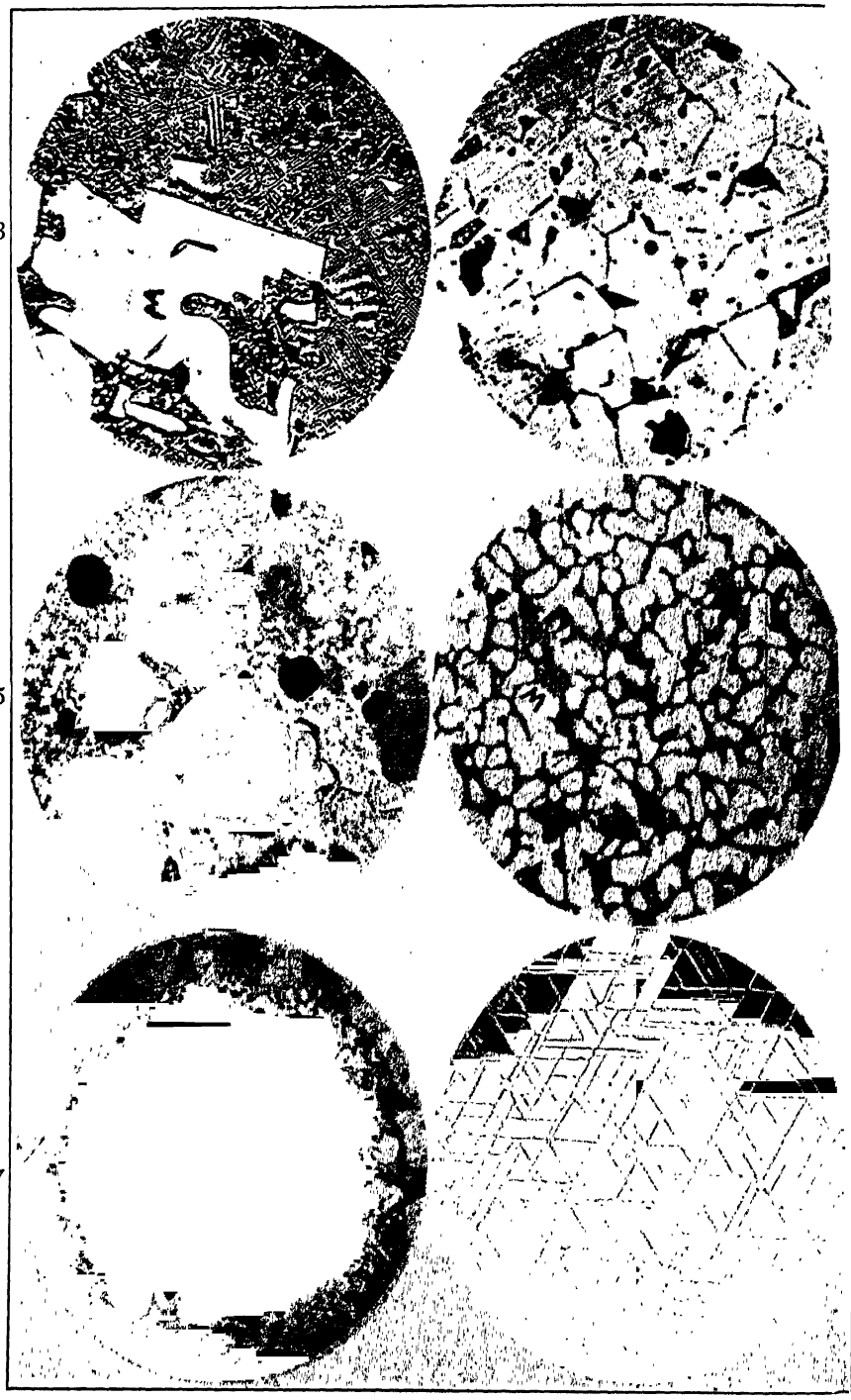
It has been noted that the iron oxide of a sinter is mainly magnetite regardless of the nature of the original ore, concentrate, or flue dust. This formation of magnetite may be explained in two ways. First, and doubtless most important, is the fact that magnetite is the stable form of iron oxide above 1200° C. Niggli[23] says that hematite when heated to 1200° C. changes to magnetite. Since the temperatures produced in sintering appear to be high, hematite presumably could not exist for any length of time. Presumably the ferrous oxide may exist as free FeO as well as combined with Fe_2O_3 to form magnetite.

Formation of magnetite below 1200° C. would doubtless result from the reducing conditions furnished by the powdered fuel mixed with the

[21] T. M. Broderick: Relations of Magnetite and Hematite. *Econ. Geol.* (1919) **14**, 353.

[22] J. W. Gruner: Magnetite-hematite-martite. *Econ. Geol.* (1926) **21**, 375.

[23] P. Niggli: Lehrbuch der Mineralogie, **2**, 141. Berlin, 1926.



FIGS. 13–18.—CAPTIONS ON OPPOSITE PAGE.

ore. A certain amount of hematite naturally develops while the sinter is cooling, as fresh air is being drawn through the sinter by suction and the reducing effect of the fuel has ceased with the completion of combustion. The possibility of some original hematite remaining in the Reading Iron Co. sinter is accounted for by the short time involved in the process.

Silicate Minerals

In the usual iron-ore concentrate silica forms the most abundant impurity. Smaller amounts of Al_2O_3, CaO, MgO are commonly present. In so far as these lesser constituents are present they are usually in the form of more or less complex silicates. Excess silica occurs as quartz. Many of the samples of sinter studied were made from ores of the East Mesabi and main Mesabi ranges in Minnesota. Grout and Broderick[24] state that quartz and amphibole [mainly actinolite $Ca(MgFe)_3(SiO_3)_4$] are the chief gangue minerals in the East Mesabi ore. Smaller amounts of garnet, fayalite, pyroxene, carbonate and other minerals are present.

Gruner[25] lists greenalite ($FeSiO_3.nH_2O$?), amphibole, chert and carbonates as the most important constituents of the iron formation up the main Mesabi range.

It is to be expected that small fragments of these minerals were present as impurities in the concentrates that were sintered. When such a mixture is subjected to heat there is a tendency for recombination of the constituents to form stable anhydrous silicates. This means the elimination of greenalite, amphibole, carbonates and free silica. Normally ferrous oxide is the only free base available for combination with the free silica, since ferric oxide does not form anhydrous silicates. There has been considerable discussion of the possible formation of iron silicate in

[24] F. F. Grout and T. M. Broderick: The Magnetite Deposits of the Eastern Mesabi Range, Minnesota. Minn. Geol. Survey *Bull.* 17 (1919) 12.

[25] J. W. Gruner: Contributions to the Geology of the Mesabi Range. Minn. Geol. Survey *Bull.* 19 (1924) 8.

FIG. 13.—RELATION OF CRYSTALLOGRAPHIC INTERGROWTH OF MAGNETITE AND SILICATE TO CRYSTALS OF MAGNETITE (*M*). MESABI IRON CO., MINNESOTA. ×300.
Presumably crystals represent iron oxide in excess of that soluble in the silicate at temperature of crystallization of magnetite. On cooling, the dissolved magnetite precipitated out to form the intergrowth. Photo by T. M. Broderick.

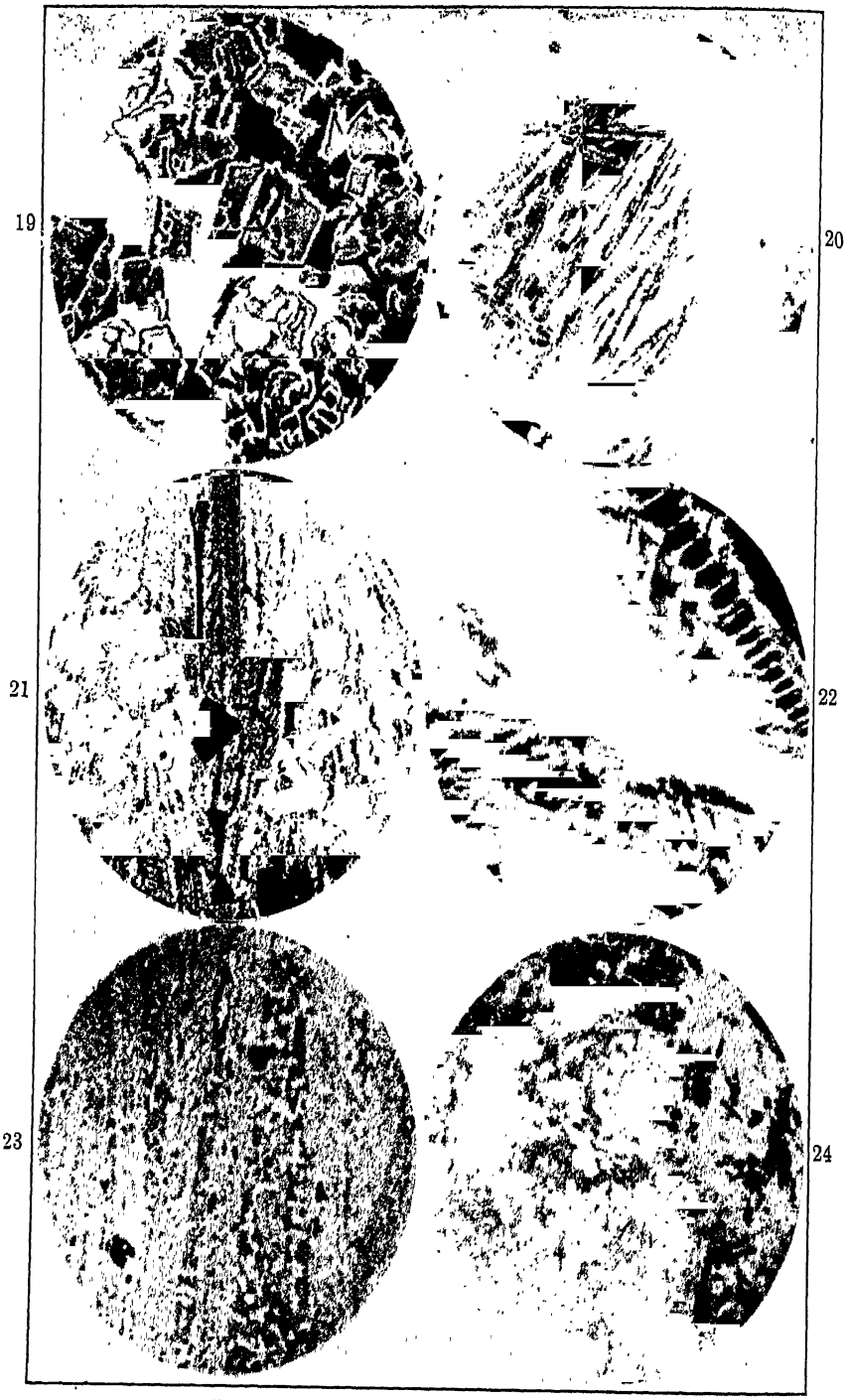
FIG. 14.—POLYHEDRAL GRAINS OF MAGNETITE IN PURE IRON OXIDE SINTER. EXPERIMENTAL SINTER. ×100.
The sinter is formed by the interlocking of the magnetite grains.

FIG. 15.—GRAINS OF QUARTZ (*Q*) REMAINING IN SINTER. EXPERIMENTAL SINTER OF PURE IRON OXIDE PLUS 25 PER CENT. SiO_2. ×100.
Examination in thin section shows reaction rims around many similar grains where fayalite is in process of formation.

FIG. 16.—GLOBULAR GRAINS OF MAGNETITE (*M*) IN SILICATE (*S*). SINTER B2. ×200.
Contrast with the normal tendency of magnetite to assume external crystal form.

FIG. 17.—HEMATITE (WHITE) DEVELOPING AROUND SIDES OF PORE AND PENETRATING MAGNETITE ALONG OCTAHEDRAL PLANES. MESABI IRON CO. ×100.

FIG. 18.—HEMATITE (WHITE) ALONG OCTAHEDRAL PLANES OF MAGNETITE. COMMERCIAL SINTER, READING IRON CO. ×200.



FIGS. 19–24.—CAPTIONS ON OPPOSITE PAGE.

sinter, and it has been emphatically stated that iron silicates did not form during the sintering process,[26] due to insufficient temperatures and to the short time involved. The writer thought from a preliminary examination of sinter submitted by E. W. Davis in 1926 that iron silicate had not formed, but detailed study of thin sections, as well as polished surfaces, proved beyond doubt that iron silicate does form abundantly and is a characteristic part of most sinter (see Figs. 20 to 24).

Where silica and iron oxide are the principal constituents of the sinter it is to be expected that ferrous silicate (Fe_2SiO_4), the natural mineral fayalite, would occur. This is proved by optical studies to be the case. The writer is indebted to Dr. R. B. Sosman of the Geophysical Laboratory for verifying the determination of this compound. The work on the system FeO-SiO_2 shows definitely that fayalite forms if equilibrium is reached. It doubtless forms as well before equilibrium is reached.

The form fayalite takes when well crystallized is a characteristic lath shape often arranged in fan-shaped groups or in clusters. Figs. 3, 4, 21, 22 and 23 show it in its well-developed form better than words can describe it. The fayalite is seldom if ever free from minute inclusions, which are probably magnetite but may be FeO. This, as noted above, is evidently a result of the separating out of iron oxide held in solution in the silicate at high temperatures. It is obvious from the manner in which nearly perfect magnetite crystals are embedded in the sheafs of silicate, as in Fig. 22, that both fayalite and magnetite represent entirely new generations of minerals formed during the sintering process. Neither magnetite nor fayalite have fragmental forms such as exist in a finely crushed ore.

---

[26] B. G. Klugh: *Op. cit.*, *Trans.*, A. I. M. E. (1912) **43**, 364.

FIG. 19.—MAGNETITE CRYSTALS WITH SHELLS OF LATER HEMATITE (WHITE). COMMERCIAL SINTER, READING IRON CO. ×300.

Probably due to oxidation during the cooling of the sinter.

FIG. 20.—THIN SECTION OF SINTER SHOWING CLUSTER OF FAYALITE (Fe_2SiO_4) CRYSTALS. COMMERCIAL SINTER, MESABI IRON CO., MINNESOTA. ×60.

Black is mainly magnetite. Note shape of crystals. Rounded structure strikingly resembles chondrules in meteorites.

FIG. 21.—THIN SECTION OF SINTER SHOWING NEARLY PARALLEL BLADES OF FAYALITE WITH MAGNETITE (BLACK) CRYSTALS EMBEDDED. SINTERED CONCENTRATE FROM SHENANGO PIT, MESABI RANGE, MINNESOTA. ×50.

Note herringbone structure of fayalite brought out by minute inclusions of magnetite along crystallographic directions in fayalite.

FIG. 22.—HIGHER MAGNIFICATION OF FAYALITE SHOWING LATH-SHAPED CRYSTALS AND MAGNETITE (BLACK) INCLUSIONS. SAME SECTION AS FIG. 20. ×100.

FIG. 23.—POLISHED SURFACE SHOWING AREA OF FAYALITE WITH FEW DENDRITIC FORMS AND NUCLEII OF MAGNETITE. SINTERED CONCENTRATE FROM SHENANGO PIT, MESABI RANGE, MINNESOTA. ×125.

FIG. 24.—CLUSTERS OF SILICA GRAINS (*S*) IN MASS OF REFUSE SINTER. POLISHED SURFACE. ×200.

Sintered mixture contained 50 per cent. SiO_2. Main mass of sinter is fayalite. Small amounts of a white constituent, probably iron oxide, are also present.

Fayalite is so abundant in iron-ore sinter that its characteristic laths were recognized in practically every sinter studied. The lathlike form is not universal, however, and often what is apparently the same mineral occurs as small irregular grains such as are the characteristic occurrence of natural olivine $(FeMg)_2SiO_4$. It is not uncommon to find the blades of fayalite in rounded clusters, as shown in Fig. 20. Dr. F. F. Grout has called attention to the striking similarity of some of these structures to the chondrules (round or oval granules usually consisting of olivine or enstatite embedded in a dense matrix of similar material) which are characteristic of some stony meteorites. The conditions resulting in their formation are perhaps similar.

Fayalite, when pure, has the formula Fe_2SiO_4 but in its occurrence in nature the iron molecule normally is isomorphous with Mg_2SiO_4, forming olivine. Natural olivines also contain varying percentages of CaO, Al_2O_3, MnO, etc. It is thus possible that the small amounts of these oxides known to be present in some sinter are in the fayalite. Small amounts of transparent minerals may be unobserved amidst so much opaque material.

The abundance and form of fayalite definitely indicate that it represents a material that has crystallized during the sintering process and not original material. The evidence, of course, is conclusive that magnetite is developed by the process, as a hematite ore when sintered becomes magnetite and whatever hematite is present is normally a new generation later than magnetite. Proof that fayalite is generated by the sintering process is furnished by a sinter prepared by Mr. Davis from pure chemically precipitated iron oxide and quartz sand. Thin sections of this sinter show a few grains of silica (see Fig. 15) remaining, but the greater part has united with iron oxide to form the characteristic lath-shaped crystals shown in Figs. 20 to 23. Reaction rims around some of the quartz grains show the incipient formation of fayalite.

To investigate the development of fayalite somewhat further, series E of the experiments listed in Table 3 were made.

To the Mesabi magnetite concentrate, of which an analysis is shown in Table 1, sufficient amounts of finely ground quartz sand were added to give a total SiO_2 percentage varying from 15 to 50 per cent. Examination of these high-silica sinters clearly showed the presence of fayalite. Higher percentages of silica give characteristic eutectic structures (Fig. 9). When the silica content is high and the particles as large as 50 mesh, complete combination of iron and silica does not take place in the limited time of sintering.

A portion of the fines of sinter E8, containing 50 per cent. SiO_2, was partially fused in a crucible and allowed to cool. Polished surfaces and thin sections showed that fayalite had developed as small crystals (Fig.

24). Iron oxide remained as very minute grains and as an intergrowth with the silicate. The temperature required was so high that complete fusion was not attained at 1500° C. but the experiment served to prove conclusively that in the presence of excess silica practically all the iron oxide present combines with the silica to form Fe_2SiO_4. This is, of course, brought out by the work on the system FeO-SiO_2.[27] When allowed to reach equilibrium the oxides combine to form fayalite.

It should be emphasized, perhaps, that fayalite was fully as characteristic of the commercial sinter studied as of the sinter produced under experimental conditions. The sinter from the plants of the Ducktown Chemical and Iron Co. and a blast-furnace flue-dust sinter from the American Ore Reclamation Co. showed particularly well-developed fayalite.

Examination of thin sections of several samples of sinter shows that not all of the silicate present crystallizes to form fayalite. In some specimens much of the silicate material is isotropic, indicating that the material is in the form of a glass rather than crystallized as a definite mineral. It is probable that in some cases this glass is the material that would have crystallized to form fayalite (fayalite is orthorhombic) if it had not been prevented by the sudden cooling of the sinter. Often the material varies from perfectly isotropic to poorly birefracting, to good crystalline fayalite in the same specimen of sinter. Some of this material may be an uncrystallized eutectic or other complex material.

The correlation of the equilibrium diagram of the system FeO-SiO_2 and the facts observed in sinter can be only very general. The exact temperatures existing at the centers of combustion can not be determined and Fe_2O_3 and Fe_2O_4 as well as FeO are present. The formation of abundant fayalite in sinter does show, however, that to a considerable degree the iron oxide present in sintering is FeO and the temperatures prevailing are above the points at which FeO and SiO_2 combine to form fayalite. Since FeO is certain to develop on account of the reducing effect of the carbon in the sintering mixture, it seems that fayalite must of necessity form in the presence of free silica. Further work on the systems involved in sinter will doubtless throw much light on the reactions involved in the sintering process. The presence of Fe_2O_3 and the compound Fe_3O_4 is of particular significance.

Structure of Sinter

The characteristic feature of a sinter in hand specimen is its porous cellular nature. This is no doubt the most important reason for the beneficial action of sinter in the blast furnace, which results in increased

[27] J. H. Whiteley and A. F. Hallimond: The Acid Hearth and Slag. *Jnl.* Iron and Steel Inst. (1919) **99**, 199.

C. H. Herty and G. R. Fitterer: *Op. cit.*

capacity and reduced fuel consumption. That this porosity continues down to microscopic size has been shown by Klugh.[28] The minuteness of some of these pores and their abundance is shown by Fig. 25, a sinter made from Mesabi hematite ore. The magnification is 100 times; the actual diameter of the field shown by the photograph is about 0.75 mm., or about half the diameter of the head of a pin. In this area there are nearly 100 pores. The importance of this porosity in admitting the reducing gases in the upper part of the furnace to intimate contact with the iron oxide to be reduced can scarcely be overemphasized.

The size and number of pores vary somewhat with conditions, but in general any satisfactory sinter has a high porosity, although not as high as the area illustrated in Fig. 25. When it was realized that porosity seemed to be by far the most important factor in the action of the sinter in the blast furnace special attention was directed to a study of this characteristic in all available samples. Perhaps the most striking thing about most sinter, regardless of variable composition, or conditions, is the uniform porosity. The following generalizations regarding porosity seem to be justified.

Hard steely specimens of sinter have high porosity in hand specimens (*i. e.*, a cellular structure), and relatively low microscopic porosity. In general these specimens have fairly high silicate content and are very well crystallized. They represent the toughest sinter examined and would stand handling the best.

Sinter high in iron with very little silicate has low porosity in hand specimen as well as microscopically.

The sinter made from pure Fe_2O_3 shows on polished surface triangular outlines of pits or pores caused by failure of the isometric crystals of magnetite to fit together exactly.

It is a general rule that areas in sinter high in silicate are low in microscopic pores. When little or no silicate is present the porosity of the entire sinter is low.

Varying the percentage of fuel and water, as was done in a series of experiments, has surprisingly little effect on the porosity. With a given ore sintered in a given machine, the porosity seems to be much the same, if the ore sinters at all.

The series of experiments in which silica was added showed high porosity both microscopically and in hand specimen, but the pores were irregular rather than round and the sinter was brittle.

Areas of small crystals and high microscopic porosity usually go together.

Some practical suggestions regarding porosity may be based on these generalizations.

---

[28] B. G. Klugh: The Microstructure of Sintered Iron-bearing Mineral. *Trans.*, A. I. M. E. (1913) **45**, 330.

Reduced porosity is likely to result when impurities or iron content are too high. About 60 per cent. iron content gives a sinter of average porosity and average toughness. In general, hardness and toughness vary with the microscopic porosity. A sinter of moderately high porosity can be made to withstand handling fairly well. Such sinter was examined from the plants of the East Mesabi Iron Co., Tennessee Copper Co., Ducktown Chemical and Iron Co., Bethlehem Steel Co. and American Ore Reclamation Co. Hard steely sinter is likely to have high coarse porosity but low microscopic porosity. One would expect that such sinter would not react quite so well because less iron oxide is exposed at a pore surface.

25 26

FIG. 25.—EXTREME DEVELOPMENT OF MICROSCOPIC PORES (BLACK). SINTERED CONCENTRATE FROM SHENANGO PIT, MESABI RANGE. ×100.
Original area has a diameter about half that of the head of a pin.
FIG. 26.—PORES SOMETIMES DEVELOP IN AREAS OF GANGUE AS SHOWN IN THIS SINTER, MESABI IRON CO., MINNESOTA. ×100.

Probably the most important factors affecting porosity are the manipulation of the sintering machine as well as the amount and type of impurity. In general, small experimental machines give less satisfactory sinter, due especially to the greater exterior surface relative to the amount of sinter. Variation in coal and water content has relatively little effect until the limits are approached at which sintering will not take place at all.

The strength of the sinter is another important factor, as it must withstand a considerable burden in the furnace. The tougher sinters were, in general, better crystallized; that is, they showed much of the texture illustrated in Fig. 6. Varying the amount of fuel and water had some effect on the strength of the sinter, as brought out in Table 3.

The prevailing microstructures observed in iron sinter are shown in Figs. 1 to 26. Usually a satisfactory sinter shows large areas similar

to Fig. 6; that is, relatively large areas of nearly perfect magnetite crystals embedded in silicate. Associated with such areas are lesser areas of dendrites and skeletal crystals of magnetite and areas of crystallographic intergrowths of magnetite and silicate (Figs. 12 and 14).

In the more friable sinter appear considerable areas of the globular texture shown in Fig. 16. This texture may be the result of high temperature with sudden cooling. This is suggested by the fact that the texture is most frequently seen in samples sintered with a high fuel content. The graphic or eutectic pattern illustrated in Figs. 9 and 10 is apparently found mainly where the silica content is high. For example, sinter E7 (Table 3) is composed almost entirely of this intergrowth. Where silicate is abundant the bladed structure illustrated in Figs. 21 to 23 is common. The crystals of magnetite are embedded in the groups of fayalite crystals. When small amounts of silicate are present it is found as a matrix or binder to the magnetite grains (Fig. 7).

Hematite, as noted above, is usually found around pores and penetrating magnetite along the octahedral planes of the crystals. It also forms shells or coatings around the magnetite crystals (Figs. 17 to 20).

Cause of Sintering

The question naturally arises as to the exact cause of sintering. The raw material consists of fine concentrate, flue dust, or other iron oxide, water, and crushed coal. The ore is usually fine, in some cases −150 mesh, but the coal is commonly crushed to about 8 mesh. During the sintering process the water and coal, with the exception of the ash, are eliminated and the ore is formed into a cellular clinkerlike mass which has a considerable crushing strength. It is thus obvious that the process produces a bonding of the material. It has been stated[29] that the iron oxide and silicates are bonded together by incipient fusion. The studies here reported do not bear out this conclusion. The photomicrographs fail to show any original fragments of either ore or silicate except in the case where sand was mixed with the ore. The microscopic study of polished surfaces of the sinters proves conclusively that the sinters are predominantly, and in most cases almost entirely, composed of a new generation of crystals or grains.

This new generation of crystals probably has formed by crystallization of material actually molten during the sintering process but recrystallization, which takes place at elevated temperatures but below the melting points of either of the constituents of the mixture, may have been effective. An important example of recrystallization is found in the metamorphism of rocks, which takes place extensively without fusion. Somewhat analogous processes may be effective in the sintering process. Which of these processes is most important, we cannot be sure, but since

[29] B. G. Klugh: *Trans.*, A. I. M. E. (1913) **45**.

the temperatures formed momentarily in the sinter by the innumerable centers of combustion are probably very high we may be justified in considering fusion and subsequent crystallization as the important process. The writer has inclined more and more strongly to this view as the investigation proceeded.

Regardless of the manner in which the process takes place, certain facts may be observed by studying sinter microscopically. These facts show the cause of the bonding of the material. These are two important methods of bonding: (1) the interlocking of grains and crystals of magnetite; (2) the binding together of the magnetite grains or crystals by silicate.

The second is apparently the most important in the average sinter. That the first is effective is shown by a sinter made by Mr. Davis from pure iron oxide. Fig. 14 shows the manner in which the polyhedral grains of magnetite are interlocked; Fig. 7 shows the manner in which small amounts of silicate act as a cement between crystals of magnetite. Where silicate is at all abundant the magnetite is completely isolated in silicate, as is well shown in Figs. 6 and 22. In so far as any original particles remain, they are undoubtedly bonded together by incipient fusion, as suggested by Mr. Klugh. The gangue minerals present, and the amounts, have a very important effect on the process. They naturally act as a flux and cause increased fluidity and thus promote recrystallization.

No experiments varying the gangue content were made except series E. It seems probable, however, that a study of the relation of gangue and fuel content necessary to sinter would show that mixtures containing considerable amounts of fluxing gangue minerals could be sintered with a low fuel consumption. This would form an interesting and perhaps a profitable field of investigation from a commercial standpoint.

Practical Results of the Investigation

Perhaps the most important result of the microscopic study of polished surfaces of iron-ore sinter is the indirect benefit which usually results from a better understanding of the fundamental changes involved in the process. It is hoped that many new facts have been brought out by this work. A number of photomicrographs have been used to illustrate exactly what was found in the way of relationships. Opinions may vary as to the interpretation, of course.

Certain suggestions of a practical nature may be made as a result of this intensive study.

It seems rather certain that a sinter which has a high degree of porosity and at the same time is tough, so that it can withstand considerable handling, is one which has had rather favorable conditions for crystalliza-

tion, so that much of the sinter appears microscopically like Figs. 4 to 7, and Fig. 25.

The presence of a reasonable amount of silicate undoubtedly gives a tougher sinter. This is due to the fact that the silicate acts as a bond and also remains molten longer than the magnetite and gives the magnetite crystals an excellent chance to form. The latter fact is clearly demonstrated by the relative perfection of the magnetite crystals in the presence of abundant silicate.

It has been shown by the series of experimental sinters that varying the amount of coal and water affects the sintering and the amount of possible variation is rather limited. There is for every ore an ideal percentage of fuel and water that will give the best results. The minimum amounts of both that will yield satisfactory sinter will be most economical. A microscopic study of sinters from a commercial plant made with varying amounts of fuel and water should quickly show the best mixture.

It has been shown that there is a tendency for oxidation to affect the magnetite during the cooling of the sinter, with the resultant formation of hematite. The formation of much hematite is not desirable, as it results in a soft earthy material which would cause losses in handling, and a flue dust. This suggests that the shorter the time of cooling and the sooner the cake is discharged the better, since oxidation of magnetite is active only at higher temperatures.[30]

The series of experimental samples of sinter indicate that magnetite as globular grains (Fig. 16) is a result of a high fuel content. Sinter with this texture is normally friable and would not stand handling well. If microscopic examination of a sinter revealed this texture a lower fuel content should be used, perhaps with a decrease in the amount of water added.

Examination of the experimental sinter made with the minimum coal possible (4 per cent.) shows that the texture is irregular. There are relatively few perfect crystals of magnetite, there is great variation in size of the grains and the silicate is filled with inclusions and intergrowths of oxide. The presence of this sort of texture would suggest increasing the fuel content somewhat, thus increasing the reaction.

It has been stated that the satisfactory action of sinter in the blast furnace is due to the porosity and a lack of iron silicate. These studies show beyond doubt that iron silicate is abundant in iron sinter, but evidently does not interfere with reduction in the furnace, at least if it does this effect is overcome by the great porosity of normal sinter. It is the writer's opinion that the favorable effect of sinter in the furnace is due almost entirely to its porosity. Part of the iron is in the ferrous

[30] J. W. Gruner: Magnetite-martite-hematite. *Econ. Geol.* (1926) **21**, 375.

state, which may have a favorable effect but probably not a very important one.

It was expected in the early stages of the work that some correlation would be found between the amount of iron silicate produced and the nature of the sintering process and mixture, as well as the percentage of fuel and water in the charge. Careful study of all sinter available clearly shows that under the conditions that produce a high percentage of sinter from the charge practically all of the silica combines to form iron silicate. The only exceptions were in the cases where SiO_2 was added to the charge to study its effect. In these samples some of the coarser fragments of quartz remained in the sinter. This was due to the fact that the short time involved in the process does not allow equilibrium to be reached. Refusing this sinter showed that fayalite was produced nearly up to the amount of iron available.

Conclusions

Only a few years ago it was generally stated among blast-furnace operators that only a limited amount of sintered iron ore could be used to advantage in blast furnaces; that when the furnace burden was increased much above 30 per cent. sinter trouble developed in the operation of the furnace. Many blast-furnace "ills" have proved to be "growing pains" and this seems to be one of them. Recent blast-furnace operations have been reported in which sinter made up the entire ore charge. The results have been exceedingly favorable, as by using the sinter it was possible to practically double the rated capacity of the furnace and materially reduce the coke consumption. It is noteworthy, however, that results recently secured by screening crude ore to a definite size for blast-furnace charges have shown radical improvements in capacity and coke consumption. This indicates that it is the porosity of the charge that is of most importance in blast-furnace operations rather than the chemical state in which the iron exists. Iron silicates, however, are difficult to reduce, and since we have definitely identified these silicates in practically all samples of sinter examined and since ordinary iron ore contains only a small amount of iron silicate, it appears that the increased porosity of the charge when using sinter is of such value to the blast furnace that the increase in the percentage of the iron silicate minerals in the sinter is far overshadowed by the increase in porosity. If good sinter could be produced containing no iron silicate this sinter would undoubtedly be better for blast-furnace use. While no method has been determined by which the amount of iron silicate can be regulated, the definite identification of this mineral and explanation of the manner in which it is formed gives metallurgists a scientifically accurate foundation from which to proceed in working out the problem of making better sinter.

By this work the sintering process has been elevated from a crude fritting process to the field of high-temperature chemistry. Practically all of the constituents of good sinter have been in the molten state and the formation temperatures of the various chemical compounds have been reached. Therefore the temperature at which sinter will again melt is considerably below the temperature at which the original constituents would melt. This may account for some of the improvements in blast-furnace practice observed when sinter is used. It may also account for the difficulties reported in blast-furnace operation when sinter and ore are mixed in the furnace burden. The rapidly melting sinter causes the slower melting ore to be carried down the furnace shaft more rapidly than is desired, therefore difficulties develop. It is suggested that further work should be done along the line of mixing fluxes with the sintering mixture. This may help materially in controlling the amount of iron silicate produced as well as in reducing the amount of fuel necessary.

Acknowledgments

Acknowledgments are due to E. W. Davis, superintendent of the School of Mines Experiment Station at the University of Minnesota, who suggested the problem and cooperated throughout.

The writer had the advantage of some preliminary work on sinter by Dr. T. M. Broderick and acknowledgment is gladly made of his important contribution. Francis G. Wells, as the writer's research assistant, made the experimental sinter and assisted in much of the work.

The work was made possible by a research fund placed at the writer's disposal by the Graduate School of the University of Minnesota.

DISCUSSION

W. P. Putnam, Detroit, Mich.—The author refers in two or three places to the porosity of the sinter as being responsible for the increased capacity of a blast furnace when using sinter only. I wonder whether or not the increased capacity is due entirely to porosity, or whether it is not in part due to the partial reduction of the Fe_2O_3 to the magnetite condition, or possibly some metallic iron, although I can find no mention in the paper about the presence of magnetic iron. I wonder if anyone has had any particular experience on that point. Unfortunately, I see no analysis of the sinter, showing the complete composition of the sinter product.

T. L. Joseph, Minneapolis, Minn.—The author says on page 47 that from 90 to 99 per cent. of the metallic mineral is present as magnetite.

G. B. Waterhouse, Cambridge, Mass.—The point was, whether any metallic iron was there, not magnetite?

J. M. Riddell, Cleveland, O.—On page 47 the author states that it is unlikely that metallic iron is an important constituent of normal sinter, and that it was not recognized in the many sinters studied.

T. L. JOSEPH.—In regard to the benefit of the sinter, there is no clear distinction in the paper between the porosity of the individual lumps and the over-all porosity of the charge. The big value of the sinter in my opinion is not due to any partial reduction, but to the fact that in sintering the particles in the charge are brought to more uniform size. Reduction to magnetite is of no great advantage as the first stages of reduction are easily accomplished in the upper section of the blast furnace. As to the effect of particle size, we know, for example, that by separating the ore into several sizes and charging each size separately the practice can be materially improved. That is because the voids in the charge are considerably increased by the process of sizing and, also, size segregation is decreased. Both of these factors favor better gas distribution. I think that the great benefit from the sinter is due to the more uniform average particle size.

Another point in the paper is with regard to the porosity of the sinter. The porosity is due inherently to the generation of gas, and as the water and coal are probably the primary sources of this gas they are important in the matter of porosity. The viscosity of the fused portion of the sinter is another feature affecting porosity.

The sintering process is different from nodulizing, in which there is no generation of gas but merely agglomeration by partial fusion.

Manganese Ore by the Bradley Process

By Carl Zapffe,* Brainerd, Minn.

(Cleveland Meeting, September ,1929)

The object of the Bradley process is to free manganese oxide from its associated gangue and separate the contained iron oxide by dissolving the manganese and precipitating it from the solution. This results in producing two oxides as concentrates, the one to be converted into a manganese sinter and the other into an iron sinter. The manganese sinter may be made to contain as high as 70 per cent. manganese and as low as 1 per cent. silica, with phosphorus not to exceed 0.02 per cent. and from that figure downward to about 0.005 per cent., and with sulfur at 0.007 per cent. The iron sinter contains about 2.50 per cent. manganese, making the total recovery of the manganese 98 per cent.

The method involves selective roasting, which converts the manganese into a form in which it is soluble in an aqueous solution of ammonium sulfate, then precipitating the manganese as a hydrate by using ammonia gas, then stabilizing and washing the hydrate, followed by sintering; concurrently most of the iron oxide is converted by roasting into an insoluble form and becomes a residue with magnetic qualities, which makes possible the recovery of much of the iron in the ore.

Leaching manganese by using sulfur dioxide gas was shown possible many years ago. Mr. Bradley tried it for a year, working in conjunction with the original experimenters of that method, and found that while relatively pure manganese oxide could be produced, the likelihood of developing a commercial process along this line was not very encouraging. He also attempted leaching with nitric and sulfur acids, but the cost of recovery mounted and the quality of the product was not as good. Mr. Bradley tried nearly every leaching method proposed, and the experiments were made on a large scale in the spacious laboratories of John C. Wiarda & Co., in Brooklyn, N. Y. Insufficient encouragement was discernible in the results obtained.

Upon the suggestion of N. Arthur Laury, of John C. Wiarda & Co., Bradley undertook using ammonium sulfate. Because a high rate of recovery appeared feasible, Bradley planned the erection of a 4-ton pilot plant at the State of Minnesota Mines Experiment Station, at Minneapolis. The results of that work are described in this treatise.

Wilson Bradley early surrounded himself with men interested in work of this kind and availed himself of associations with such men as Dr. Charles A. Doremus, Dr. E. P. Mathewson, N. Arthur Laury, men of the Dorr Company at Westport, Conn., and, finally, H. A. Brassert & Co., consulting engineers of Chicago. A. J. Boynton, Vice President of the latter company, devoted a great deal of time to investigating every step and every piece of apparatus Bradley offered as a component part of a system, and then prepared a design for a plant of commercial scale. In a letter addressed to the Bradley-Fitch Co. dated March 15, 1929, A. J. Boynton writes:

> Our study of the technology involved has extended over a period of a year or more, and has covered every feature of operation and equipment. We believe the process to be technically correct and practically controllable. The apparatus required is standard in the metallurgy of the higher metals, and is obtainable from firms of high commercial and engineering standing. We regard the process as experimental only with respect to adjustment of details of construction and operation.
>
> We recommend the process as an unusual opportunity for developing a highly profitable business.

The description that follows incorporates data contained in a report prepared by H. Brassert & Co. accompanying its design of a commercial plant. Inasmuch as considerable interest has been created by Bradley's work, which has extended over a period of five years, and because until now the inventor has not permitted the publication of any descriptions of his work, this treatise has been planned to present considerable detail, which procedure may lead readers to the belief that the method and the plant are complicated; instead, the method is simple and the apparatus is standard in every respect.

The Process by Steps

The fundamental features of the process are: making both a manganese ore and an iron ore; effecting a separation of manganese and iron by means of selective roasting; leaching the manganese from the roasted ore by using ammonium sulfate; precipitating the manganese by using the ammonia gas generated during leaching; fixing the precipitate by oxidizing with air; breaking down and reforming the ammonium sulfate, so that daily very little additional ammonium sulfate beyond that originally charged into the system is required; washing the manganese precipitate and the iron-silica residue and evaporating the liquor to conserve the dissolved salts in the moistures of these two products and to reduce the sulfur content; drying the precipitates; magnetic wet-concentration of the iron-silica residue; sintering the manganese and the iron concentrates. These several features may be conveniently described in five steps.

Step No. 1, Ore Preparation

The ore will in all probability be crushed at the mine, but can be crushed at the unloading track hopper, using a jaw crusher, to pass a 4-in. ring. In the plant it will pass over a vibrating screen, and the coarser material will be crushed again to minus ¼-in. in a Symons cone crusher. From this point it is assumed that the operation will be continuous and constitute a 24-hr. service. The capacity of a given plant should be considered in terms of manganese sinter rather than raw ore, and the capacity of the auxiliary services should be equal to maintaining a full production of manganese, the amount of crude material required varying with the content of manganese in the crude material.

Leaching action was found to be preferably conducted with material which will pass through a 65-mesh screen. This reduction in size is best performed by grinding wet, on account of lessened cost and avoidance of dust, for which a Hardinge ball mill and a standard Dorr classifier has been used. Grinding fine and classifying is a closed circuit.

The overflow from the classifier goes to a Dorr thickener and thence to a vacuum filter, by means of which it is proposed to reduce the moisture content in the ore to perhaps 10 per cent. With this percentage the material will be easily handled. The filter cake will be discharged by means of a belt conveyor into a storage bin, from which it drops by gravity feed into a drying kiln.

The methods and equipment referred to above have been standardized by long practice, and no difficulties in design will be encountered. In the next steps the equipment used is fully developed mechanically and presents only problems of size and proportion, due to the novelty of its proposed use, in order to secure the desired capacity.

Step No. 2, Drying and Reduction

The ore having been properly prepared, it is next roasted in a reducing atmosphere, using blast-furnace gas or partly burned water gas, or producer gas, at a temperature of about 750° F. The reasons for the procedure in this step are of a chemical nature. The process is applicable to ores containing the minerals pyrolusite, psilomelane and manganite, which are oxides, and rhodocrosite, the carbonate of manganese, which would in the roasting be changed to an oxide. Rhodonite, the silicate of manganese, can only be reduced at very high temperatures, and much the same is true of braunite (Mn_2O_3), and reduction at temperatures over 800° F. is undesirable. The purpose of this step is to convert manganese to the monoxide (MnO), because it is completely soluble in ammonium sulfate whereas the higher oxides are not soluble; also, by using the lower temperature (not to exceed 800° F.), most of the iron present in the ore is not changed to the ferrous oxide (FeO) but becomes

Fe_3O_4, the magnetic form. In the ferrous state iron is soluble in ammonium sulfate in aqueous solution; and, under favorable conditions, will be acted upon in a manner similar to manganese, which would involve further treatment to separate the manganese from the iron. Such treatment is possible, of course, but it is less convenient and more expensive than is the separation in preliminary roasting. Selective roasting, therefore, made possible avoiding certain inconveniences in the leaching step and made possible the recovery by magnetic concentration of a valuable by-product of iron ore.

The experimental work showed that, at a temperature not exceeding 800° F., MnO_2 will be reduced to MnO, and Fe_2O_3 will be reduced to Fe_3O_4 with a comparatively small production of free FeO, the latter corresponding to 10 to 20 per cent. of the total iron present, which is in a measure desirable. It has also been discovered that the reduction to MnO precedes that of iron to FeO, and the latter substance does not form until nearly all the manganese is in the form of MnO. This selective roasting is a discovery by Bradley, others having failed because they used higher temperatures.

The reducing roast may be carried on in a Wedge-type, multiple-hearth furnace, in a rotary kiln or in other types of apparatus in which the ore may come into contact with reducing gas and in which a maximum temperature of 800° F. is mechanically possible. Inasmuch as an intimate contact between ore and gas is desirable, a furnace has been designed which makes possible lifting the ore burden in small quantities and dropping it when the ore buckets reach various heights as they revolve within the furnace, and thus combine the advantage of easy control of gas obtainable with a Wedge furnace and the economy of gas inherent in the rotary kiln, and enables better regulation of speeds. The shell of the furnace designed does not revolve; also lower power consumption is obtained. The flow of the ore through the furnace is countercurrent to the flow of the gas.

The gas used for reduction may be any reducing gas containing carbon monoxide or hydrogen. In the operation of the pilot plant water gas was used, and equally good results have been obtained with blast-furnace gas. In the case of water gas, selectivity of reduction was promoted by the presence of water vapor in the gas. With blast-furnace gas no additional moisture is necessary beyond that ordinarily carried in washed gas; but unwashed hot gas will be preferable to washed gas.

Because of the exothermic reactions, the gas temperature in the kiln increases from inlet to outlet. This is regulated by introducing little gas at first and adding cold gas as temperature increases. This is not possible with a rotary kiln.

The processes of preheating and of reduction after grinding are proposed to be carried on in two kilns, of which the one for drying and

and preheating will be an ordinary rotary kiln. Preheating is adopted because the hot gases from the reducing furnaces are available. It will be fired by the hot, partly oxidized gases coming from the reducing kiln and a 40 per cent. reduction in the ore is thus obtained, which becomes a substantial economy. The drying kiln is fed by wet ore coming from the pressure filter, and this dried or preheated ore is discharged into the second or reducing kiln. The speed may be regulated to slow or fast advancement of the ore, and it may require less than 45 min. to pass a ton of ore through the reducing kiln, which is 60 ft. long and 10 by 10 ft. in cross-section.

The velocity of the gas in the drying kiln must be kept low in order to avoid dust losses. The escaping gases may go directly to the stack or they may be subjected to a gas-washing operation, either by means of a Vortex cleaner or a wet-washer of the tower type. An alternative possibility lies in the construction and use of a scrubbing tower for wet-washing. In this case the Dorr thickener used to thicken the ore after grinding may be used, and the recovered dust deposited therein pass with the primary ore to the drying kiln from the reducing system. In any event, it is a matter of only a minor economy and is not essential at the outset. It is mentioned merely to indicate that dust recovery presents no difficulties if one wishes to attempt it.

It has been estimated that if blast-furnace gas is used, the following approximate composition will carry on the process of reduction: CO_2, 12.56 per cent.; CO, 25.12 per cent.; H_2, 3.29 per cent.; N_2, 55.65 per cent.; H_2O, 3.38 per cent. It is assumed that this gas is received at the burner of the reducing chamber at a temperature of 60° F. and a barometric pressure of 30 in. A portion of this gas is used for combustion—approximately 3669 cu. ft. (16.6 per cent.). This is burned with air in a Steinbart burner. The heat derived from this combustion is used in raising the remainder of the blast-furnace gas to a temperature of 750° F. The composition of this gas after combustion and the fresh gas mixed with it will be as follows:

	Before Reduction, Per Cent.	After Reduction, Per Cent.
CO_2	15.99	26.00
CO	20.03	10.01
H_2	2.62	1.31
O_2	0.01	0.01
N_2	58.01	58.01
Water vapor	3.34	4.66

The estimated rate of use of gas is 22,023 cu. ft. per ton of ore treated, based on using only one-half the reducing power of the gas. This quantity is in excess of that actually required in tests made.

Calculations show that the requirements for heating and drying are 717,408 B.t.u. per ton of ore in the natural state. The total heat released in the reactions per ton of ore reduced is 358,154 B.t.u. The total sensible heat in all gases available for drying and evaporation becomes 1,525,583 B.t.u. Allowing for a 5 per cent. loss of heat and deducting the units required for preheating and drying, the sensible heat in gases leaving the drying kiln is 731,896 B.t.u., for which some use may be found.

Step No. 3, Leaching and Precipitation

In actual operation leaching the manganese is a step apart from precipitating the manganese; but from the chemical standpoint, leaching and precipitating follow each other so closely that the two steps may also be conveniently considered together. The simplicity of this step is apparent because leaching and precipitating manganese from one ton of ore requires only 30 minutes.

The reduced ore taken from the roasting furnace, after being cooled partly out of contact with air, is dumped into ammonium sulfate liquor, the latter having a temperature of about 190° F., as it is obtained from evaporators which are in the circuit. The resulting action is known as digestion, and the tank in which it takes place as a digester. The digester consists of three shallow trays, and is equipped with paddles revolving on a vertical central shaft, for the purpose of promoting contact between ore and liquor in each tray.

The manganous oxide in the roasted ore is dissolved in the liquor and becomes manganous sulfate. This reaction generates ammonia gas, which is withdrawn by an exhauster and piped to two ammonia towers, or precipitators, for further use. The reaction is represented by equation 1:

$$MnO + (NH_4)_2SO_4 = MnSO_4 + 2NH_3 + H_2O \qquad (1)$$

The manganous sulfate is in solution. After clarifying the solution of any residual ore, and having captured the ammonia gas released in the reaction, sprays of the liquor and the ammonia gas are brought into contact in standard ammonia towers and manganous hydroxide is precipitated, according to reaction 2:

$$MnSO_4 + 2NH_3 + 2H_2O = (NH_4)_2SO_4 + Mn(OH)_2 \qquad (2)$$

The manganous hydroxide is immediately treated with atmospheric air. This is accomplished by entering atmosphere on the minus pressure side of the ammonia-gas exhauster and allowing the air to mix with the ammonia gas, the oxidation occurring in the towers as precipitation takes place. This changes the manganous hydroxide to partly dehydrated manganic hydroxide, according to the reaction 3:

$$2Mn(OH)_2 + O = 2MnO.OH + H_2O \qquad (3)$$

In this form the precipitate is stable and becomes heavy enough to be settled, then washed, dried and sintered. The application of atmospheric air in changing the unstable manganous hydroxide to a stable precipitate of manganic hydroxide was a point developed by Bradley.

The reversibility of the first two reactions makes it possible to re-use the ammonia. The losses are very slight, and are due to possible occasional leakages of the gas and to the ammonium sulfate which the moisture in the manganese hydroxide, before sintering, may have in solution. These losses are unimportant. The possibility of the continuous use of ammonium sulfate in a recurring cycle is a feature which makes the process commercially feasible. Only a small addition of fresh solution of ammonium sulfate is made daily, and that is done to obtain better results in a single step to be described later. The practical conditions under which the regenerative leaching and precipitating cycles operate constitute one of Bradley's basic discoveries.

Leaching and precipitation are both produced by the reversible chemical reaction. The direction in which the reaction proceeds depends on the degree of concentration of manganous sulfate in the liquor and on the excess of ammonium sulfate present and its temperature. Control of the process is accordingly secured by the order in which the flowing liquor encounters the metals and the ammonia gas. It is desirable that the liquor going to the precipitators shall contain a maximum of manganous sulfate and a minimum of ammonium sulfate. In this condition its susceptibility to reaction with ammonia gas is at a maximum and, consequently, manganese may be most readily precipitated.

To make precipitation more nearly complete and to make use of both weak and strong ammonia vapors generated, two precipitators are used. The weaker ammonia vapors are used in the precipitator receiving the more heavily charged liquor and the stronger ammonia vapors are used in the precipitator receiving the partly extracted liquors received from the first precipitator.

For leaching, two digesters are provided. Final leaching, which involves the removal from the ore of all the manganese possible, takes place in the second digester. The ore coming to this digester has had approximately 60 per cent. of its manganese removed in the first digester. The manganese in the ore which reaches the second digester is so limited in quantity in comparison with the large volume of liquid solvent used, that the most complete leaching possible takes place without greatly reducing the leaching power of the liquid. The partly saturated solvent in this second digester flows to the first digester, where it encounters fresh ore and leaches 50 to 60 per cent. of the manganese, and then passes to the precipitators where the manganese is removed. Accordingly the flow of liquor is from the secondary digester to the primary digester and thence to the precipitator; whereas the flow of the ore is

from the primary to the secondary digester and thence to a residue tank. During digestion the surface of the liquid should be as large as possible and the depth a minimum. Using a tray type of digester, the depth of the liquid can be varied from 6 to 18 in., and the time of detention can be easily regulated.

Leaching of manganese is 50 per cent. or more complete before the leaching of iron commences. This fact operates to prevent the leaching of iron in the primary digester. It is also a law of this leaching process that where iron has been leached, it will be removed from the solution and replaced by manganese in the presence of a large excess of the latter, such as exists in the first or primary digester. Such iron as is, therefore, leached in the second digester, may be thrown down as ferrous hydroxide after reaching the first digester. Iron so eliminated from the leaching liquor is not reabsorbed, but becomes part of the residual ore to be removed from the primary digester.

Manganese precedes iron in leaching, wherefore iron precipitates more rapidly than manganese from the leaching solution. If necessary, by adding a little ammonia immediately before the liquor reaches the precipitator, an iron precipitate could be made in advance of the precipitation of manganese. This is offered only to show what could be done, but is not contemplated, and illustrates the flexibility of the procedure as well as the ease of the control of this step. Iron is, however, removed, or fixed by selective roasting, as already described, and the digesters are relieved of this additional function.

The second of Bradley's basic discoveries relates to the practical conditions under which the regenerative leaching and precipitating cycle operates. The chemical reactions were described by Laury, and in general the cycle is protected by his patent, under which the Bradley-Fitch Co. has the sole rights. The cycle is correct as to reactions, but was discovered by Bradley to be operative only in the presence of a large excess of ammonium sulfate solution. The proportions of ammonium sulfate and manganous sulfate in the leach liquor at various points in the cycle forms the subject of one of Bradley's patent claims.

Another important feature developed by Bradley in operating his pilot mill was to digest his ore in two stages, with the precipitators interdisposed between. The liquor withdrawn from the precipitators, which at this stage is richest in ammonium sulfate and leanest in manganese, flows to the second digester where it meets the partly leached ore conveyed to it from the first or primary digester. In the second digester the leaching of the ore is completed, but the liquor is now only partly enriched with manganese and is, therefore, piped to the primary digester where its saturation with manganese is accomplished by working on untreated material. From the primary digester the liquor flows to the precipitators, and then the cycle begins anew. Manganese is accord-

ingly precipitated at the point of maximum load, and the final leaching is accomplished at the stage of minimum manganese content of the liquor.

This leaching step results in two products. The principal product is the precipitated manganese hydroxide in the precipitators, which is discharged into a large settling tank. The other product is a residue, taken from the secondary digester, consisting of iron oxide—chiefly in the magnetic form (Fe_3O_4) resulting from roasting, and silica. This is received in the so-called iron-silica residue tank. Both products are in the form of finely divided ore. It has now taken 1 hr. 45 min. to run one ton of ore through the preheater, the reducing furnace, the digesters and the precipitators.

Step No. 4, Washing and Drying

Both the manganese-bearing precipitate and the iron-silica residue resulting from the leaching operation require washing. One reason is to reduce the final moisture to a point which permits sintering; another reason is to reduce the valuable contents of the moisture contained in the final product to a negligible quantity; and another is to avoid an excessive sulfur content. The amount of water necessary for washing is the most important point in this step because this water takes on ammonium sulfate and is returned to the system, and mingles with returned sulfate-bearing liquor from other sources, and necessitates an equivalent evaporation to maintain the concentration of the liquor of the system at the most economical point. The ability to wash with a low water consumption may accordingly overbalance considerations of low first cost or of labor required with other methods, wherefore so far it seems that washing is best carried out with a vacuum filter and final drying by using a waste-heat dryer, concluding with 18 per cent. residual moisture as a content suitable for sintering.

Step No. 5, Magnetic Concentration of Iron Residue

From the iron-silica residue referred to, a large part of the magnetic iron is recovered by means of magnetic concentration and forms an ore with 58 per cent. or more of iron. So far a magnetic log-washer has been used, but a Grondal wet separator may prove equally applicable. Inasmuch as some FeO is made in the reducing oven and travels through the mill with the manganese, not all the original iron reaches the iron-silica residue tank, nor could it be recovered magnetically as iron ore. Allowing for the customary tailings product in all iron ore concentrating work, it will be possible to recover in this step at least 70 per cent. of the total iron content of the crude ore. Silica content of the ore will be below the customary limit at which penalties are invoked.

In some particles of ore there is a certain mechanical combination between iron and manganese which the process will not separate. As a result, the iron concentrates will contain around 2½ per cent. manganese. On the other hand, the total recovery of manganese in the whole process becomes nearly 98 per cent.

Step No. 6, Sintering

For metallurgical purposes it will be necessary to sinter both the washed manganese hydroxide and the iron oxide by-product. The manganese precipitate, after being dried with waste heat, exhibits a peculiar cohesiveness and breaks up into lumps of a size which makes sintering extremely easy. Sintering the magnetic iron concentrates has been demonstrated to present no difficulties. The moisture content of the ore must be closely controlled to obtain the best results, but such control is, fortunately, easy to obtain.

Miscellaneous

Evaporation of water added to the system is also provided. Plenty of waste gases are available for the production of steam, wherefore a simple type of direct evaporator is all that is required. One evaporator is planned for the return liquor from the primary digester-manganese hydroxide circuit and another for the secondary digester-iron hydroxide circuit. Other equipment consists of piping for the flow of liquors and gases, tanks for storage or subsidence, pumps for liquor and exhausters for gas.

The only piece of apparatus in the entire plant which is mechanically novel is the reducing furnace which has been designed, and it is merely an improvement over other types as to control, economy and more thorough reduction. It is an easy matter to develop in a plant the several circuits required because so much of the material handled, after leaving the reducing furnace department, is solids in suspension in liquids, or liquids only and gases which may be shunted around through piping, and in and out of apparatus set at various elevations with respect to each other and where most practicable.

Operating Statistics

A plant of commercial size is not yet in operation, but a complete design has been prepared for its construction. At this moment there is at hand some data determined for a plant which was calculated to produce 50 tons manganic hydroxide per 24 hr., or its equivalent in manganese sinter, and I shall use the quantities given for the various stages of such a plant.

We may begin by using 250 long tons of ore per day, requiring two reducing furnaces, each of 125 ton capacity. They will operate as long

as is necessary to produce enough roasted ore to keep the balance of the equipment operating the full 24 hr. The crude ore used and the roasted ore produced were as follows:

	Crude Ore Dried 212° F. Per Cent.		Roasted Ore, Lb.	
Mn	15.00	MnO_2	7.39	Mn = 67.14 lb. or 20.56 per cent.
Fe	27.50	MnO	80.60	
SiO_2	24.56	Fe_3O_4	156.90	Fe = 115.98 lb. or 35.45 per cent.
Al_2O_3	2.50	FeO	3.87	
CaO	1.00	SiO_2	66.10	
Combined water	8.90	Al_2O_3	11.67	
Moisture	.....		326.53	

That is, 326.53 lb. of roasted ore was delivered to the primary digester per min., of which 3.87 lb. is FeO which will travel with the MnO and 7.39 lb. is MnO_2 which will travel with the Fe_3O_4.

The primary digester receives 5000 lb. ammonium sulfate liquor per min., coming from the secondary digester, and it contains 10 per cent. or 500 lb. ammonium sulfate and 4.12 per cent. or 206 lb. manganese sulfate.

The contents of the primary digester pass into a primary thickener from which the solids are taken that supply the secondary digester, whereas the effluent liquor is conducted to the ammonia towers. This liquor measures 5387 lb. per min. and contains 7.17 per cent. or 386 lb. of ammonium sulfate and 6.03 per cent. or 325 lb. of manganese sulfate. Here is noted an increase in manganese sulfate content (325–206) of 119 lb. with a loss in ammonium sulfate.

The liquor passes to the towers, where the manganese is precipitated, after which it is piped to a storage tank and drawn from the latter at the rate of 4967 lb. per min., containing 11.49 per cent. or 571 lb. ammonium sulfate and 2.96 per cent. or 147 lb. manganese sulfate. The solids that settled weigh 105 lb. and 59.6 per cent. or 63 lb. of it is metallic manganese, 1.87 per cent. or 1.95 lb. is metallic iron, and 1.00 per cent. or 1.05 lb. is silica. This material is piped to the manganic hydroxide thickener, and the sediment is the product later washed, dried and sintered.

Every 24 hr. 50 tons of manganic hydroxide and 80 tons of 10 per cent. solvent liquid is drawn off, the latter being recovered and sent to the evaporator and then into the secondary digester.

The secondary digester uses as its feed the material which has been partly acted upon in the primary digester. The liquid effluent from the manganic hydroxide thickener is part of the solvent used, being drawn at the rate of 5200 lb. per min. and containing 568 lb. or 10.92 per cent. ammonium sulfate and 147 lb. or 2.83 per cent. manganese sulfate. To make the digestion of the manganese as near complete as possible, fresh

ammonium sulfate is added to the mixture in the secondary digester, thus providing an excess desired and which takes care also of variations in the composition of the ore.

The material drawn from the secondary digester is piped to a thickener and the solids there formed constitute the iron-silica residue. The digester discharges into this thickener at the rate of 5235 lb. per min. The liquor contains 9.55 per cent. or 500 lb. ammonium sulfate and 3.94 per cent. or 206.5 lb. manganese sulfate, which is the liquor piped to the primary digester for further loading with manganese. The solids consist of 4.68 lb. Mn., 156.9 lb. Fe_3O_4 or 112.97 lb. Fe, 65 lb. SiO_2 and 11.67 lb. Al_2O_3, which is washed, dried, concentrated and sintered.

The ammonia gas generated in the two digesters is captured and piped to the second stage precipitating tower, where it is used to make the final precipitation of manganous hydroxide from the ladened liquors conducted to that tower. This gas, at 60° F., has been estimated as follows per minute,

	From Primary Digester	From Secondary Digester	Combined
NH_3	26.78 lb.	13.39 lb.	40.17 lb.
Volume	594.00 cu. ft.	296.00 cu. ft.	890.00 cu. ft.

What takes place in the two digesters may be shown by setting down in columns the weights of the materials for each:

	Primary		Secondary	
	Lb.	Per Cent.	Lb.	Per Cent.
Liquid drawn off per min	5387		5235	
Sulfates in solution:				
Ammonium sulfate	386	7.17	500	9.55
Manganese sulfate	325	6.03	206	3.94

	Solids Precipitated per Min. from This Solution by NH_3 in Precipitators, Lb.	Solids in the Residue Taken from Secondary Digester per Min. Lb.
Mn	63.00	4.68
Fe	1.95	112.97
SiO_2	1.05	65.00

Production Statistics

The ores used in testing the process came from nearly every well-known manganese-bearing area in the United States, but the procedure was the outcome of work involving primarily the siliceous manganese-bearing formation which is so very abundant in the Cuyuna iron ore district of Minnesota. The material used had this composition:

	Dried at 212° F., Per Cent.	Natural State, Per Cent.
Mn	15.00	13.50
Fe	27.50	24.75
SiO_2	24.56	22.10
Al_2O_3	2.50	2.25
CaO	1.00	0.90
Combined water	8.90	8.01
Moisture		10.00

Attention may be directed especially to the content of manganese, iron and silica, the combination of iron and silica alone being unfavorable for use of this material as a manganiferous iron ore.

The compositions of the manganese sinters are made whatever the product should be. The sinter may contain 70 per cent. Mn; but if standard grade ferromanganese is to be manufactured therefrom, the inclusion of iron, at the expense of some manganese, is most desirable. While the objective in experimenting was still only obtaining a high-manganese sinter, the analyses of the sinter obtained were like the following, with manganese often being nearer 70 per cent. and iron and silica under 2 per cent.: Mn, 67.31 per cent.; Fe, 4.83 per cent.; SiO_2, 2.67 per cent.; P, 0.012 per cent.; Al_2O_3, 0.35 per cent.; MgO, 0.16 per cent.; C, 0.235 per cent. In making ferro, about one unit of iron is required for each eight units of manganese. The inclusion of 7 per cent. of iron in the manganese sinter to be made will conserve this iron, which, being nonmagnetic, would otherwise be lost in the tailings. It will also permit the necessary silica for the blast furnace operation to be obtained, as now, as low-grade siliceous iron ore, which is the cheapest and most desirable form possible. For these reasons the composition of the sinter was made as follows: Mn, 63.58 per cent.; Fe, 7.06 per cent.; SiO_2, etc., 2.00 per cent.; P, less than 0.02 per cent.

Beginning with an ore containing 13.50 per cent. manganese natural and having a recovery of virtually 92 per cent. of it in only the manganese hydrate made, it requires 5.199 tons of crude ore to make one ton of manganese sinter. For every such ton, 1.5254 tons of iron concentrate is made as a by-product, analyzing about 58 per cent. iron and 2.57 per cent. manganese, and 1.345 tons of waste. In a cost set-up credit would be taken for this by-product, the unit value of which would vary with the conditions of the sale but being at least 8 to 8½ c. per unit of iron plus manganese. The output of the plant designed is doubled by doubling the ore reduction.

The scope of this process, both mechanically and chemically, is not dependent on whether the crude ore analyzes as shown herein or is of lower metallic content. In ores much higher in manganese than 13 per cent. and correspondingly lower in iron than 25 per cent., the cost per ton of sinter necessarily becomes less. Obviously, the richer

the material the better, but this process is inherently suited to highly siliceous material. One can say that the lower the iron and the higher the silica, the better. An important feature is that phosphorus is virtually eliminated in the treatment, and this feature alone may have great bearing in the adoption of the process.

Due to the excess of ammonium sulfate always present Bradley's process adapts itself to nominal variations in the composition of the crude material, and a lowering of several per cent. in the manganese content and a raising of the silica content in the crude material would not affect the plant operation. The passage of the ore through the plant need not

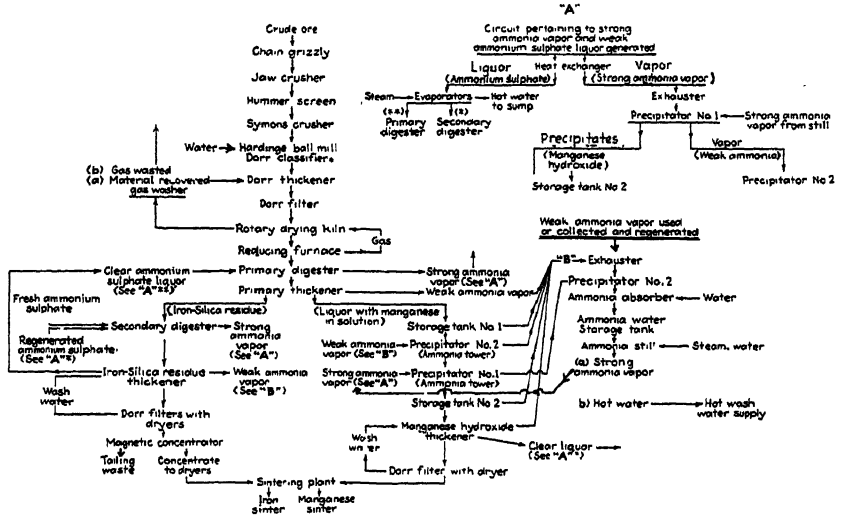


FIG. 1.—FLOW SHEET OF BRADLEY PROCESS FOR LEACHING MANGANESE ORES.

be regulated for small variations in manganese content, or iron or silica. If regulation is needed, it will be in pump strokage, for maintaining density of pulp sent to filters and not to regulate leaching.

The grade of the crude ore to be used will eventually be fixed by what material is readily available, and what material is cheapest to obtain. The process is applicable to low-grade manganiferous ores situated in other parts of the United States other than the Cuyuna district of Minnesota provided the right oxide minerals of manganese constitute the components of the ore. It is interesting to note that basic slag containing 8 to 9 per cent. metallic manganese has also been experimented with and 85 per cent. of the manganese was recovered.

It has been estimated that if the manganese sinter described is used for making 80 per cent. ferromanganese, the following proportions of materials would be required: Sinter, 1.534 gross tons; iron ore, 0.018 gross tons; limestone, 0.388 gross tons; coke, 2.000 gross tons. The iron

ore prescribed is assumed to be cheap high-silica ore, used chiefly for the purpose of controlling the composition of the slag.

Mr. Boynton has estimated that in a run of 24 hr., the consumption of blast-furnace gas would be 7,347,787 cu. ft. for reduction of the ore and 3,973,200 cu. ft. as fuel for steam for evaporation and miscellaneous purposes. The fresh ammonium sulfate requirement per day is estimated at 967 lb., water requirement at 367,850 gal., and electric current at 9331.2 kw.-hr. The number of men required to operate the machinery used in the several steps described herein, exclusive of those needed to operate a sintering plant, is estimated at 10, or less, per shift. Mechanics, electricians and common labor may be added to whatever extent circumstances may require from time to time. A chemist will be needed on every shift.

Fig. 1 is a flow sheet illustrating the several steps referred to. The simplicity of the operation is reflected by the simplicity of the pattern of the flow sheet.

DISCUSSION

W. P. PUTNAM, Detroit, Mich.—Will that process work on carbonate ore?

C. ZAPFFE.—Yes.

W. P. PUTNAM.—Lime?

C. ZAPFFE.—I think a large amount of lime will cause trouble, but manganese carbonates containing lime are being roasted, starting with 36 per cent. manganese in the crude ore and producing nodules that contain 56 to 57 per cent. manganese, which is high.

W. P. PUTNAM.—Does it depend on the amount of lime?

C. ZAPFFE.—When working with a carbonate containing 36 per cent. manganese, there is not much chance for lime being present in amounts of consequence.

W. P. PUTNAM.—I understand there are quantities of siderite ores containing lime in fairly large percentages.

C. ZAPFFE.—If the lime content is high, there is liable to be trouble.

A. H. HOBLEY, Washington, D. C.—The plan would be to operate the Bradley process as an auxiliary to some kind of an existing plant?

C. ZAPFFE.—That would be my idea. It would give you the benefit of proximity to cheap gas supply, and the chances are there would then probably be less of complicating features of other kinds.

A. H. HOBLEY.—How about the uniformity of the product?

C. ZAPFFE.—It is extremely uniform. It does not make any difference if the ore varies several per cent. as it comes out of the reduction furnace, because there is always an excess of ammonium sulfate in the digesters which takes whatever manganese is available. If the ore runs 10 per cent., it will get 10 per cent., and if it comes 15 per cent., it will attack the 15 per cent. The strength of the solvent is regulated in the

first instance to fit the particular ore. If the ammonium sulfate solution is too strong it does not work so well; a weak solution is more satisfactory.

A. H. HOBLEY.—Would it require any closer control of the ore than is ordinarily exercised in an ordinary blast furnace?

C. ZAPFFE.—The gas control, both as to volume and temperature, has to be close, and for that reason there has been designed a type of furnace which is a combination of existing types, adopting the good qualities of all existing types. That is the only point at which it is felt that close attention is necessary.

G. B. WATERHOUSE, Cambridge, Mass.—Of course, Major Hobley realizes that all the ore is crushed to −65 mesh. A uniform size is treated, which the blast furnace does not do.

A. H. HOBLEY.—I know very little about it. I am just trying to cover some of the points that I can see would exist in competing with the present situation. The steel companies appear to prefer foreign supplies of manganese, both on the basis of cost and the uniformity of the material.

G. B. WATERHOUSE.—That is because in that way they can get a fairly uniform manganese ore, running we will say, 53 or 54 per cent. If by this method they could get a uniform manganese running roughly 70 per cent. they would be further ahead. Mr. Joseph you must have watched this to some extent.

T. L. JOSEPH, Minneapolis, Minn.—No; I believe, however, that this is probably the most important process in sight for treating ores that contain around 13 per cent. manganese, and I think Mr. Zapffe is right in that the experimental part of it has been pretty well demonstrated. The remaining point to prove is the matter of economics, which involves a large number of things and is different for different situations.

Gas-solid Contact in the Shaft of a 700-ton Blast Furnace*

By S. P. Kinney† and C. C. Furnas,‡ Minneapolis, Minn.

(New York Meeting, February, 1929)

The efficient operation of a blast furnace depends primarily upon efficient contact between the descending stream of solid materials and the ascending stream of gas. A program of research dealing with the interior of the present-day furnace is being carried by the U. S. Bureau of Mines along two lines: (1) observations on commercial furnaces and (2) experiments in the laboratory.

Through the courtesy of the officials of the Illinois Steel Co. it was possible to make a detailed investigation of the interior of the shaft of No. 4 furnace at the company's South Works, South Chicago, Ill. The experimental work is reported in a U. S. Bureau of Mines bulletin[1] which will include the results of several thousand observations on the interior of the shaft of this furnace. Such of the data as are presented later in this paper constitute only a brief summary.

The second part of the work has been conducted in the laboratory. Only one phase of the laboratory investigation has been completed at the present time, namely, the flow of gases through beds of broken solids.[2]

The object of this paper is to correlate the results of the two different lines of research and to present a more or less complete picture of the condition of the interior of a blast furnace by giving approximate, quantitative data of the actual size-distribution of solid particles in a typical furnace, and of the efficiency of contact between the gas and solid phases.

With such data before him the operator or the experimenter not only has a much better idea of the actual conditions inside a furnace, but he also knows in what direction to look for possible improvement.

The discussion which follows presents only a few of the items studied and reported; those persons who are particularly interested in all the results of this investigation must refer to the aforementioned publication.[3]

---

* Printed by permission of the Director, U. S. Bureau of Mines.

† Metallurgist, U. S. Bureau of Mines.

‡ Associate Physical Chemist, U. S. Bureau of Mines North Central Experiment Station.

[1] S. P. Kinney: The Blast Furnace Stock Column. U. S. Bur. Mines *Tech. Paper* 442, (1929) 148 pp.

[2,3] C. C. Furnas: The Flow of Gases Through Beds of Broken Solids. Bur. Mines *Repts. of Investigations*, Ser. 2904 (1928) 20 pp. Also in process of publication as Bur. Mines *Bull.* 307 (1929).

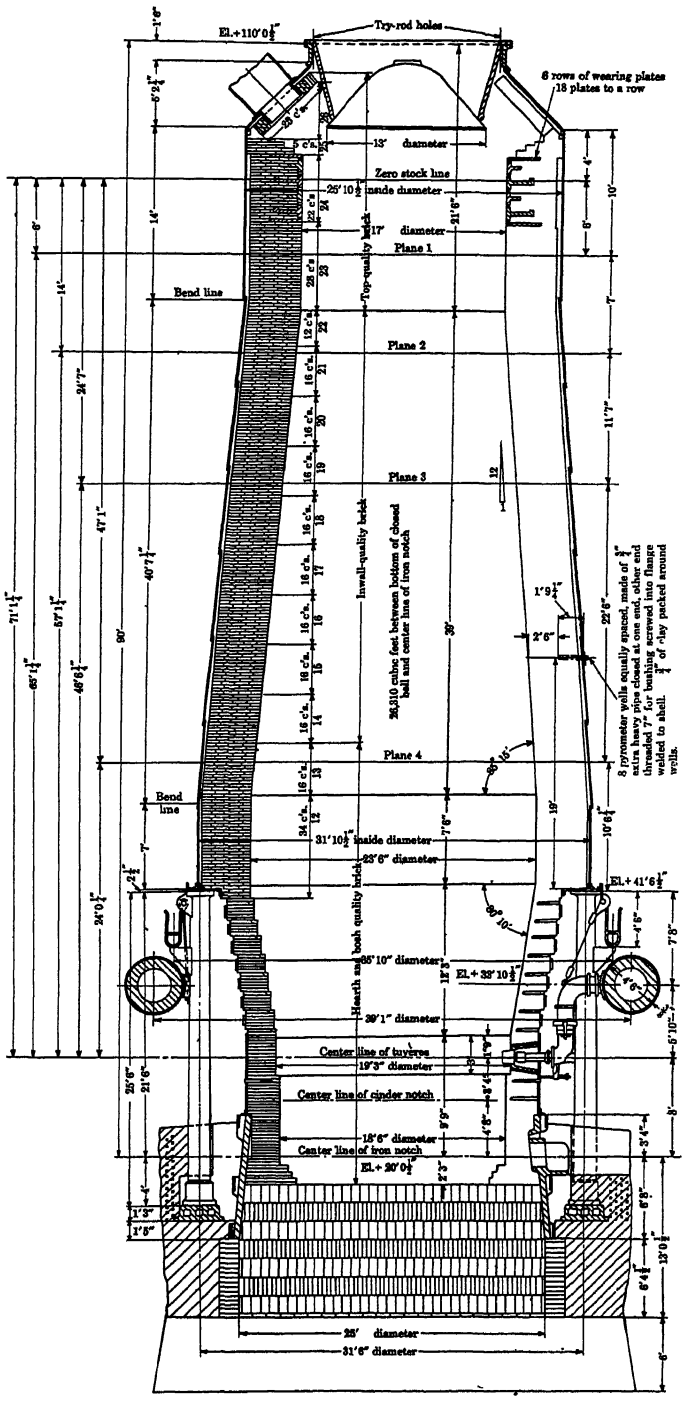


FIG. 1.—SECTION OF No. 4 FURNACE, ILLINOIS STEEL CO. SOUTH WORKS, SOUTH CHICAGO, ILL.

Furnace Observations

The lines of the furnace investigated are shown in Fig. 1.

Gas samples, gas velocity, and temperature data were taken from the inwall to the center on four different planes; plane 1, 3 ft.; plane 2, 11 ft.; plane 3, 21 ft. 7 in.; plane 4, 44 ft. 1 in. below the normal stock line. The normal stock line was 3 ft. below the zero stock line.

The samples and observations were obtained by means of tubes driven into the furnace through holes in the inwall. The temperatures were taken with thermo-couples encased in iron pipes. Gas velocities were obtained by means of specially constructed water-cooled Pitot tubes; the tubes were later calibrated under laboratory conditions and, when a factor was applied, were found to give a true measure of gas velocities in the interior of beds of broken solids. The gas samples were taken over mercury with water-cooled sampling tubes. Complete details of the work will be published later.

Gas Stream Data

The data obtained for the different planes are summarized and given in Figs. 2 to 5 which are self-explantory.

Fig. 2 shows the gas velocity at various planes in feet per second. It will be observed that, in general, the gas velocity is fairly high along the wall, drops off to a minimum at about 2 ft. from the wall, and then rises to a high velocity at the center. The higher velocity along the wall was probably caused by the batter. In plane 1, which is above the line of batter, there is no high wall velocity; the maximum velocity is almost 6 times the minimum.

The temperatures at the corresponding positions in the furnace are given in Fig. 3. It will be observed that in a general way the temperature curves follow the gas-velocity curves.

Fig. 4 shows the carbon dioxide content of the gases at the different planes. It can easily be seen that the carbon dioxide content bears some inverse relation to the gas velocity; that is, where the gas velocity is high, the CO_2 content is low, especially in the center of the furnace. One explanation of this fact probably is that where the gas passes through the stock at a high rate it does not have time to do its work of reducing the ore, and hence a part of the potential reducing power of the gas in that section of the furnace passes on unused; or, it might be that the charge is distributed so that little iron oxide is present in the center of the shaft at this elevation, but due to channeling, a large excess of gas exists. At any rate it can be seen that variations in the gas velocity across a given plane in the furnace—that is, channels—tend to cause an inefficiency in operation.

Fig. 5 shows the static pressure at the different planes. In general the greater static pressure is in the center of the furnace.

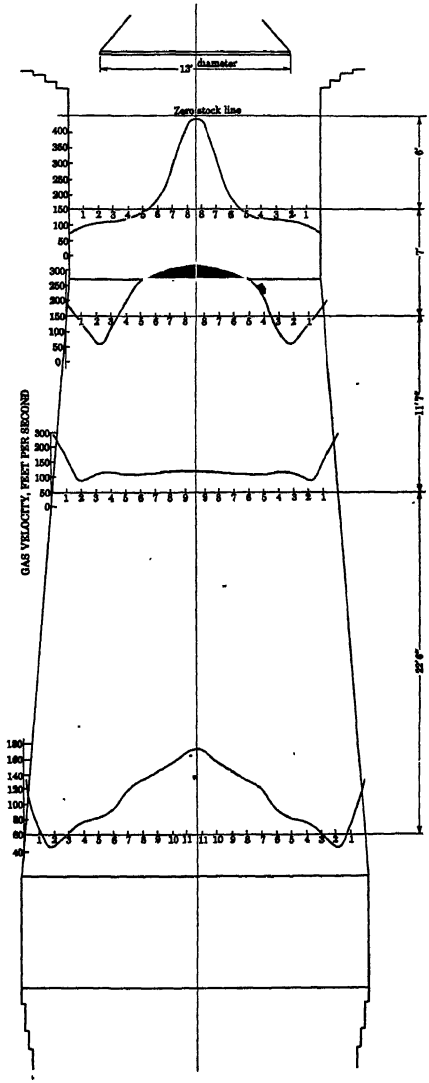


FIG. 2.—GAS VELOCITY AT VARIOUS PLANES, FEET PER SECOND.

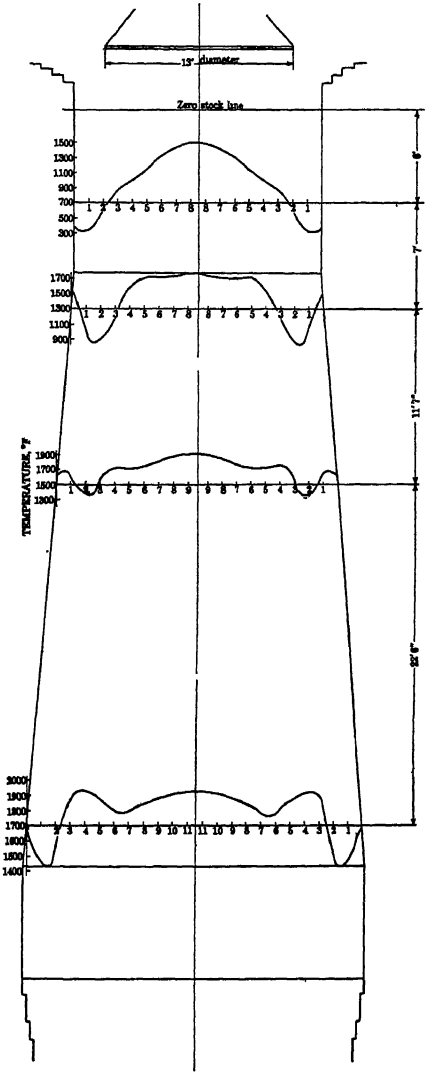


FIG. 3.—TEMPERATURES AT VARIOUS PLANES, °F.

By using the gas velocity, temperature, and pressure data, it is a simple matter to compute the rate of gas flow in cubic feet per square

foot of area under standard conditions of 32° F. and 29.9 in. of mercury. The results of such computations are shown in Fig. 6. Although the rate of gas flow under standard conditions varies considerably in different

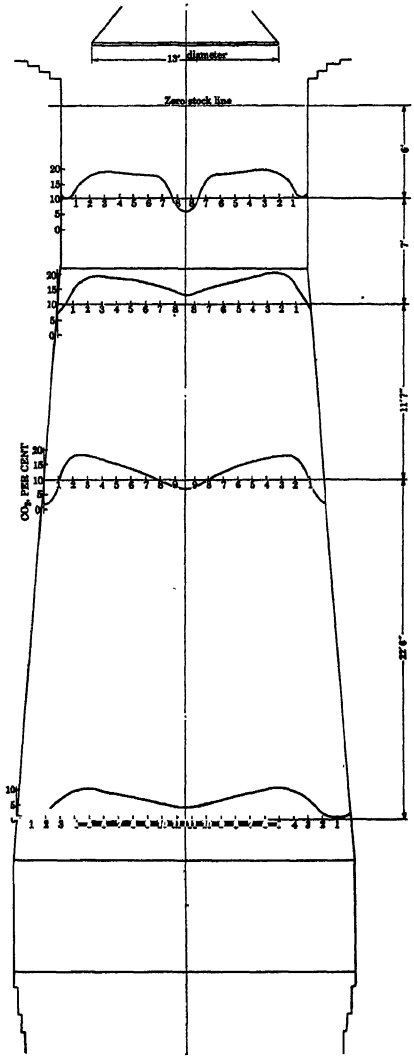


FIG. 4.—CARBON DIOXIDE CONTENT OF GASES AT VARIOUS PLANES.

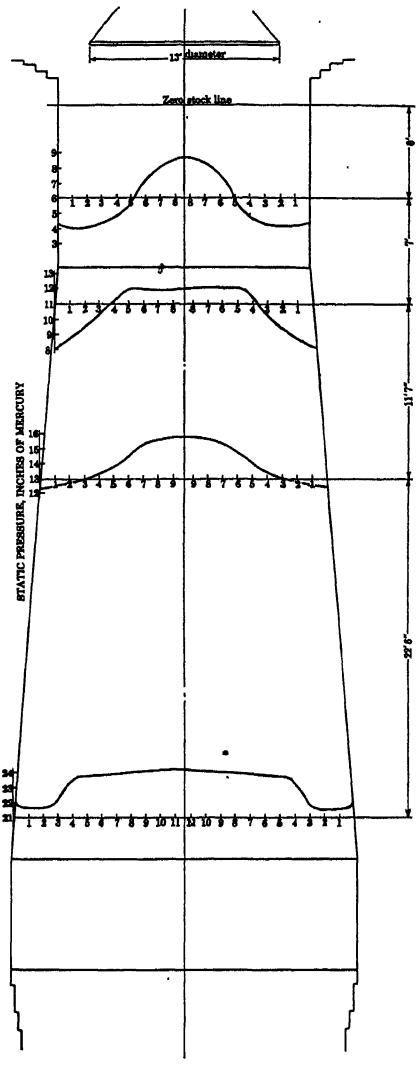


FIG. 5.—STATIC PRESSURE AT VARIOUS PLANES, INCHES OF MERCURY.

parts of the plane, the variation is not as marked as was the velocity, due, of course, to the fact that high temperature always accompanied the high velocity.

Size of Solid Particles

All of the observations in this work were on the gas phase. It would have been desirable to obtain a great many samples of the solid materials from different parts of the furnace, but experimental difficulties prevented satisfactory work of this kind. However, by using the fundamental information obtained from the laboratory study of the flow of gases through beds of broken solids,[4] it is possible to take the data obtained on the gas stream and to compute the average particle size at different points in the furnace.

The only data needed beside those already given are the pressure drops per unit of height of the furnace. These data can be obtained from Fig. 7, which shows the average pressure at the different planes in the furnace.

The complete statement of the laws of the flow of gas through beds of broken solids[5] is quite complicated. The original work involved the detailed study of nine different variables—namely, size of particle, composition of gas, temperature of gas, voids in the bed, shape of particle, size composition of bed in systems of mixed sizes, rate of flow of gas, size of container, and the amount of moisture in the bed. All of this is reported at considerable length in the complete work. However, for average blast-furnace conditions a sufficiently accurate approximation is obtained by the use of the simple equation:

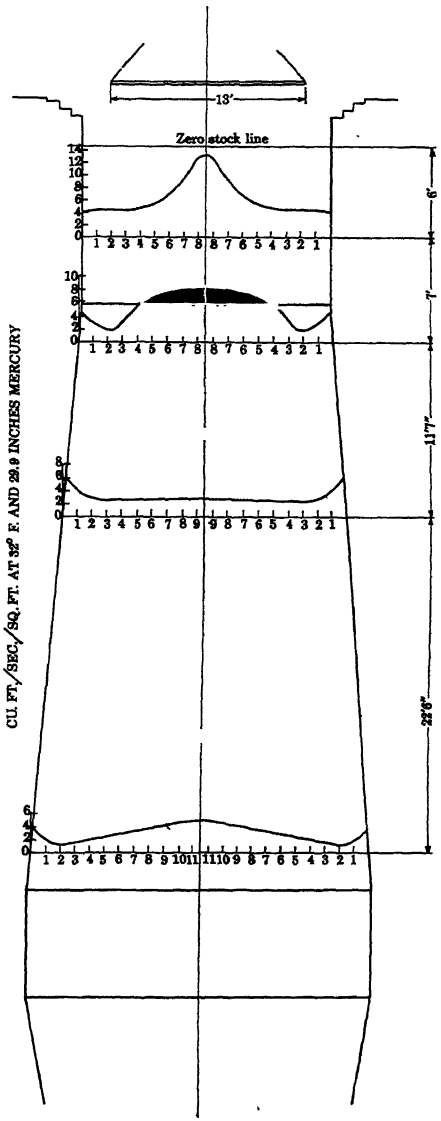


Fig. 6.—Rate of gas flow at various planes measured in cu. ft. per sq. ft. per sec. at 32° F. and 29.9 in. mercury.

$$\Delta P = \frac{1965 T^{0.15}(0.0305R)^{B}}{Pd^{1.2}}. \qquad (1)$$

[4,5] C. C. Furnas: *Op. cit.*

Where ΔP = the pressure drop per unit length of column,
T = temperature in degrees Farhenheit, absolute,
R = rate of flow in cu. ft. per sq. ft. per sec. under standard conditions of 32° F. and 29.9 in. of mercury,
$B = 3.96 - 0.72 \log_{10} T$, (2)
P = total pressure in inches of mercury,
d = average diameter in inches.

Everything is known in equation 1 except the diameter of particle d; that is, ΔP is the slope of the curve in Fig. 7; T is obtained by adding 460

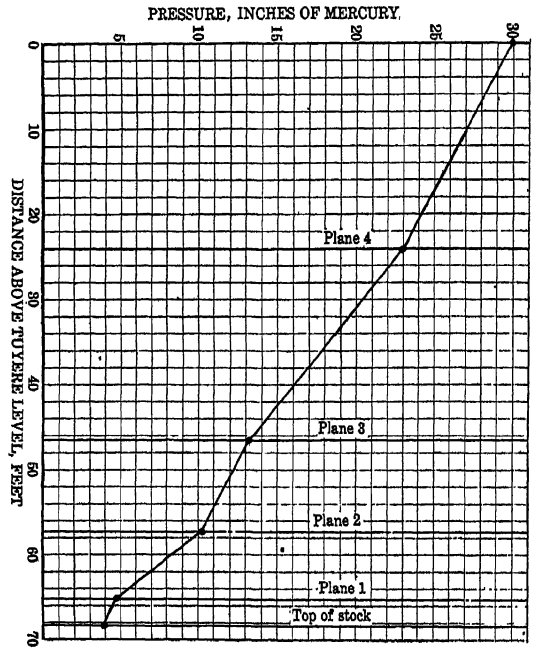


FIG. 7.—STATIC PRESSURE AT VARIOUS ELEVATIONS, INCHES OF MERCURY.

to the values obtained from Fig. 3; R is the rate of flow shown in Fig. 6; B is obtained by substituting the temperature data in equation 2; the total pressure P is obtained by adding 29.9 to the static pressures of Fig. 5.

With all of these data at hand it is possible to solve equation 1 for d, the particle size. The equation becomes

$$d = \sqrt[1.2]{\frac{1965 T^{0.15} (0.0305 R)^{B}}{P \times \Delta P}}. \quad (3)$$

The solution is simple, involving only substitution of the correct figures, raising the numbers to the specified powers, performing the

indicated multiplication, division, and extracting the 1.2 root of the product, all of which can be done quickly and easily by the use of logarithms.

The value of d so obtained is the average diameter of the particles.

By laboratory experiments it has been found that when fine particles in the bed are lifted by the gas stream, as is the case in all furnaces using fine ores, they offer practically no resistance to the passage of the gas stream. Therefore the particles finer than about 14 mesh (this figure has been determined by laboratory experiment) are automatically ignored by the computation and thus do not enter into the average.

The results of the computation of particle size are shown in Fig. 8, where average particle size is plotted against distance from the inwall for the four different planes.

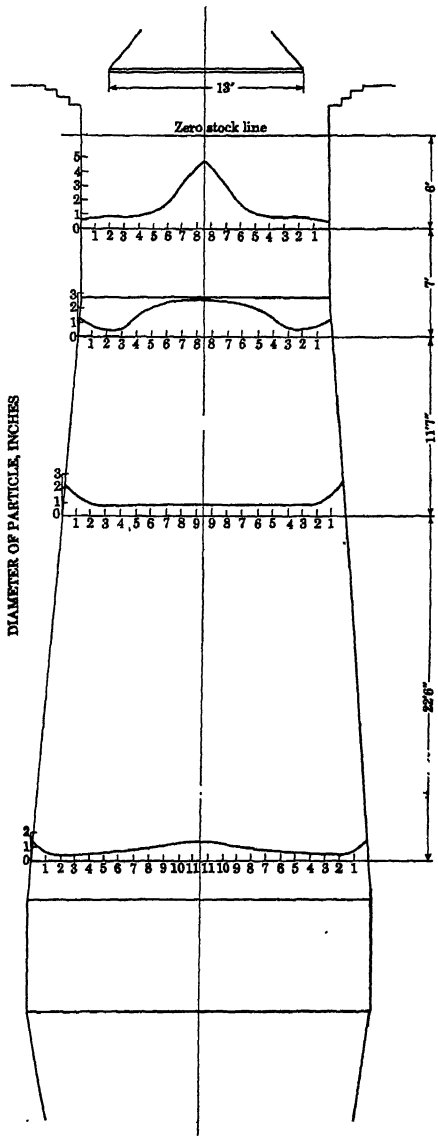


FIG. 8.—COMPUTED AVERAGE PARTICLE SIZE AT VARIOUS PLANES, IN INCHES.

MOVEMENT OF STOCK

These curves (Fig. 8) show a number of things. Plane 1, which is but 3 ft. below the normal stock line, shows an enormous disparity in particle size from the inwall to the center. This means that the charging condition in this particular furnace leaves much to be desired, as the large pieces roll to the center and leave an undesirably large chimney at that place. As the particles progress down through the furnace the discrepancies in size at different points in the plane largely disappear, until at plane 3, 21 ft. 7 in. below the normal stock line, the particle size is practically uniform most of the way across the plane. This shows that despite the poor size distribution at the top, the nonuniformity is largely straightened out in the upper 20 ft. of the furnace.

The curves of planes 2, 3 and 4 show a sudden increase in particle size close to the inwall. It is probable that this is actually not an increase in size but an increase in the percentage of voids in the bed occasioned by the batter of the furnace which tends to induce a loosely packed condition next to the wall. Equation 3 does not differentiate between particle size and percentages of void in the bed; it is probable, then, that increase in size at these points is only apparent.

A study of the group of curves as a whole shows that the stream lines of flow of the solid stock are fairly well defined. On comparing planes 1 and 2 it will be seen that an interchange of particle size has taken place, due to stock descent toward the tuyéres, and has resulted in mixing the sizes so that the average size of the particles 2 to 3 ft. from the wall in plane 2 is very small. In like manner the very large particles in the center of plane 1 have begun to flow toward the inwall in plane 2, so that the average particle size in the center of plane 2 is markedly smaller but at points 3 to 4 ft. from the center is considerably larger than in plane 1. This same effect can be seen to be continued down to planes 3 and 4. The logical interpretation of this is that the solid materials are flowing as if through a funnel of which the center is directly above the combustion zone in front of the tuyéres and directly below a point a short distance off the inwall. This is in accord with former investigations[6] on the subject which indicate that the combustion zone extends on the average but 40 in. beyond the nose of the tuyéres and that the stock tends to feed into this zone.

This is further substantiated by stock-flow measurements in the furnace. The average rate of flow for 3 points next to the wall was 3 in., whereas the rate of flow at or near the center was 2.1 in. per minute.

An interesting point is that these stock-flow measurements also substantiate the belief that the column of stock is submerged in a bath of slag and metal because of a definite pendulum-like motion of the stock column at the reception of each charge.

Improvement in Practice by Uniform Size Distribution

The foregoing data give a picture of typical conditions in the gas and solid phases in the shaft of this furnace. It can easily be seen in a qualitative way that in this furnace the mutual contact between gas and solid is not uniform. The curves of particle size in planes 1 and 2 show that the condition might be partly remedied by placing the materials more uniformly on the top of the stock.

---

[6] G. St. J. Perrott and S. P. Kinney: Combustion of Coke in the Blast-furnace Hearth. *Trans.*, A. I. M. E. (1923) **69**, 543.

P. H. Royster and T. L. Joseph: Effect of Coke Combustibility on Stock Descent in Blast Furnaces. *Trans.*, A. I. M. E. (1924) **70**, 224.

W. Von Vloten: Die Verbrennung in Gestell des Hochofens. *Stahl u. Eisen* (1893) **13**, 26.

Following a suggestion made in a Bureau of Mines publication[7] several years ago, the Columbia Steel Co. of Provo, Utah, now divides the ore into three different sizes and charges each size separately. This tends to cut down the size segregation on the top of the column and gives more uniform contact between gas and solid throughout the shaft. This practice has enabled the company at Provo to cut down the coke consumption by several hundred pounds. However, ores containing a great deal of fine material can not be sized successfully.

Uniformity of Gas Flow

Although Fig. 2 (gas velocity) and Fig. 6 (rate of flow under standard conditions) give a picture of the way the gas stream distributes itself in the furnace, they do not give a real answer to the question: How uniform is the gas flow? There is always a particular advantage in being able to point to a single figure and say: This is a measure of the quantity in which we are interested. Therefore a more or less arbitrary coefficient of uniformity of gas flow has been devised to fill this need.

Uniformity Coefficient

If the flow were perfectly uniform, there would be no variation in the rate of gas flow at different points in the plane. Let us consider perfectly uniform flow in a given cross-section plane to be represented by the figure 1.00. Then nonuniform flow across the plane will be represented by a figure less than 1.00. Rates of flow, either greater or less than the average, contribute to non-uniformity. At those points where the flow is less than the average, the co-efficient of uniformity is arbitrarily assumed to be the ratio of the actual rate of flow to the average rate of flow. At those points where the flow is greater than the average, the coefficient of uniformity is the ratio of the average rate of flow to the actual rate; that is, the coefficient can never be greater than 1.00. The coefficient of uniformity for an entire cross-sectional plane in a furnace is simply the average of the different individual coefficients for all the different units of area.

This uniformity coefficient as defined is arbitrary and requires some justification. Undoubtedly as knowledge on the subject increases some better derivation of a coefficient can be found, but after careful consideration the authors feel that the coefficient just described is the best that can be devised with the present knowledge and that it does have considerable qualitative significance.

For simplicity, utility, and clarity a coefficient of uniformity should have three properties: (1) A value of 1.00 for perfectly uniform flow; (2) a

[7] P. H. Royster, T. L. Joseph and S. P. Kinney: Influence of Ore Size on Reduction. *Blast Furnace & Steel Plant* (1924) **12**, 274.

value of zero when the rate of flow is zero (this is equivalent to saying that in a system where no gas is being introduced there is no contact between new gas and the solid, which of course is true); (3) and it should be as nearly correct quantitatively as is possible. The simplest scheme which satisfies conditions (1) and (2) is that of using ratios of velocities, as has been done with this coefficient. No quantitative data are available to tell how efficiency of reduction varies with rates of flow of gases, but it is known, in general, that the efficiency of transfer of any entity—such as molecules of gas, a liquid, or of heat—varies as some power of the ratios of the velocities of quantities involved. Therefore a ratio function may be expected to be better than one not involving ratios of velocities.

A clearer explanation is as follows: The average rate of flow of a gas stream through a furnace may be chosen as 10, for convenience. There is one part of the furnace where the rate of flow is only 1. According to the above definition the uniformity coefficient at this point is $\frac{1}{10}$. This means that that portion of the furnace is only 10 per cent. efficient in affording opportunity for gas-solid contact, for if the rate of flow over the entire furnace were only 1 it would take a furnace 10 times as large to get the same amount of gas through in a given time. In this same furnace there may be a section with a rate of flow of 20. The uniformity coefficient here according to the arbitrary definition is $\frac{10}{20}$ or $\frac{1}{2}$. This means that that portion of the furnace is inefficient, for the gas goes through so rapidly that it does not complete all of its work of reduction and heat transfer—only half completes it; that is, the given amount of gas only accomplishes half as much as it would have accomplished if it had gone at the average rate of speed, which will be considered as the ideal rate. A gas stream that is going slower than the average is inefficient because it wastes time, and a stream faster than the average is inefficient because it does not complete its task—comparable in effect to the undesirable qualities of very slow and very fast workmen.

The average coefficient for the whole plane requires some explanation. The furnace was studied in annular rings of uniform width from the inwall to the center. Since a ring 1 ft. wide at the wall represents so much more area than a ring 1 ft. wide at the center, in order to get a true average of all of the uniformity coefficients in a given plane it is necessary to multiply the uniformity coefficient of a given ring by its area, add all of these products for the entire area, and then divide this sum by the area of the entire plane. This is simply giving equal weight to all the units of area in the plane.

The quantity used for computing this coefficient is the flow of gas per unit of area as measured in cubic feet per second per square foot of area under standard conditions of 32° F. and 29.9 in. of mercury. Table 1 gives the computation of this coefficient for plane 1; the computations

TABLE 1.—*Data for Computation of Coefficient for Uniformity of Gas Flow for Plane 1, 6 Ft. Below Normal Stock Line, No. 4 Furnace, South Works, Illinois Steel Co.*

Number of Annular Ring	Distance from Inwall to Center of Ring		Area of Ring	Rate of Flow per Cu. Ft. per Sq. Ft. per Sec. at 32° F. and 29.9 In. Mercury	Uniformity Coefficient for Annular Ring[a]	Uniformity Coefficient Times Area[b]
	Ft.	In.	Sq. Ft.			
1	0	3	25.92	4.12	0.851	22.10
2	0	9	24.34	4.77	.985	24.00
3	1	3	22.78	4.91	.982	22.30
4	1	9	21.21	4.87	.991	21.10
5	2	3	19.63	4.75	.985	19.30
6	2	9	18.07	4.57	.948	17.10
7	3	3	16.49	4.28	.889	14.63
8	3	9	14.92	4.13	.852	12.70
9	4	3	13.35	4.02	.831	11.10
10	4	9	11.78	4.31	.894	10.50
11	5	3	10.22	4.66	.966	9.89
12	5	9	8.64	5.23	.924	7.98
13	6	3	7.06	5.87	.823	5.82
14	6	9	5.51	7.07	.684	3.76
15	7	3	3.92	9.72	.496	1.94
16	7	9	2.36	12.25	.394	0.93
17	8	3	0.78	13.08	.369	0.30
Total.....			226.98			205.45
Average[c] rate of flow for whole plane.....				4.83		

Note.—Coefficient of unformity for entire plane $= \frac{205.45}{226.98} = 0.902$ or 90.2 per cent.

[a] If the gas flow is less than average, the uniformity coefficient is $\frac{\text{actual flow}}{\text{average flow}}$. If the gas flow is greater than average, the coefficient is $\frac{\text{average flow}}{\text{actual flow}}$.

[b] Computed in this manner for convenience. The coefficient for each ring should be multiplied by the area of the ring and divided by the total area, and then all factors should be added. This procedure is equivalent to multiplying each factor by its area, then adding and dividing the sum by the total area, as has been done.

[c] Average rate of flow $= \frac{\text{total gas flowing}}{\text{area of plane}} = \frac{1096}{226.98} = 4.83$ cu. ft. per sq. ft. per second.

indicated give a coefficient of uniformity of 0.902 or 90.2 per cent., despite the high velocity in the center.

When the uniformity coefficient for the various planes is computed as indicated, the results given in Table 2 are obtained.

TABLE 2.—*Coefficient of Uniformity of Gas Flow for Different Planes*

Plane No.	Distance below Normal Stock Line	Coefficient of Uniformity, Per Cent.	
		Computed from Rates of Flow under Standard Conditions	Computed from Observed Gas Velocities
	Ft. In.		
1	3 0	90.2	81.1
2	11 0	70.5	65.2
3	21 7	79.5	79.7
4	44 1	74.7	75.7
Average for entire furnace.....		78.7	75.4

The last column of Table 2 shows the results obtained by computing the coefficient of uniformity from the gas velocity data rather than the rate of flow under standard conditions. The results are closely related, and it probably makes little difference which quantity is used for the computation of the coefficient, though the standard rate of flow has the better logical basis.

Table 1 indicates that, despite the great variations in rates of flow in different parts of a given plane, the average uniformity throughout the furnace is 75 to 80 per cent., perfect. This result is rather surprising in view of the great variations in velocity and flow indicated in Figs. 2 and 6. The explanation lies in the fact that the points of greatest discrepancy in rate of flow lie where the area per unit of width of annular ring is small. This statement may be amplified by saying that for a 17-ft. stock line a ring 1 ft. wide extending in from the wall has as much area as a ring 4 ft. wide at the center (this would be a circle of 4-ft. radius). Or, if a circle 17 ft. dia. were divided into three rings of equal area, the central one would be a circle with a radius of 4.91 ft.; the second ring would be 2.03 ft. wide; the third, 1.56 ft. wide. Considering the 6-in. rings of Table 1, the innermost ring has an area of 0.78 sq. ft. and the outer ring of 25.92 sq. ft., an increase of 3,300 per cent.

The surprisingly high figures for the uniformity coefficient show that a single curve giving rates of flow across a plane really conveys no idea of the uniformity of flow if uniformity is considered in the light of total volume involved. It will also be seen that a narrow strip of high velocity next to the wall is as disastrous to the uniformity of flow as a wide strip of similar velocity near the center.

As was stated before, the coefficient of uniformity of gas flow is more or less arbitrary, but it gives a definite figure to aid in forming a picture of the interior of the furnace, and it probably has a considerable significance. Sufficient data are not available to correlate this figure and furnace practice, but as more data on other furnaces are gathered, some

such correlation will undoubtedly appear; eventually it should be possible to state definitely what the ideal conditions are for the most efficient contact between the gas and solid phases in the blast furnace.

Future Work

The U. S. Bureau of Mines hopes to continue its blast-furnace investigations in the field and in the laboratory. Furnaces with different characteristics and operating conditions from those of the one discussed in this paper have been studied. The work in the laboratory is continuing in the form of a study of heat transfer from gas streams to beds of broken solids and of the rates or reduction under furnace conditions. It is hoped that eventually a more or less complete quantitative picture of the furnace may be obtained such as will enable the investigators to offer intelligent criticisms and suggestions.

Acknowledgments

The authors wish to thank the officials of the Illinois Steel Co., who have made it possible to obtain these data. Acknowledgment is also made to T. L. Joseph, supervising engineer of the North Central Experiment Station of the U. S. Bureau of Mines, for his assistance in the preparation of this paper.

[For a report of the discussion of this paper see Mining and Metallurgy (1929) **10**, No. 267, 138.]

*

Blast-furnace Filling and Size Segregation*

By C. C. Furnas† and T. L. Joseph,‡ Minneapolis, Minn.

(Cleveland Meeting, September, 1929)

It is well known that particles of different sizes are not distributed evenly throughout the average charge in an iron blast furnace. Just how great the disparity in particle size in different parts of a single plane in a furnace may be is indicated by the results of some recent investigations[1,2] conducted by the Bureau of Mines on a furnace operating on Lake ores. The wide variations found in gas velocity, gas composition, and temperature from the periphery to the center of the upper charge column were caused by the great variation in particle size of the raw materials used and were also greatly influenced by the methods of charging. This paper summarizes the results of an investigation of the influence of different methods of charging and of the treatment of raw materials upon the size distribution of the solid particles in the blast furnace. A more complete report will appear later as a Bureau of Mines technical paper.

Importance of Gas-solid Contact

One of the authors has pointed out in a previous report[3] that the operation of the blast-furnace process is entirely dependent on contact between the gas stream and the solid particles in the stock. The gas stream carries the necessary heat as well as the carbon monoxide molecules that do the work of reduction. In the parts of the furnace in which there is little or no contact between the gas stream and the solids there can be little work of reduction. Obviously, the part of the apparatus that is not doing the work for which it is intended is inefficient; the ideal condition is one in which all portions of the stock column are

* Published by permission of the Director, U. S. Bureau of Mines.

† Physical Chemist, U. S. Bureau of Mines, North Central Experiment Station.

‡ Supervising Engineer, U. S. Bureau of Mines, North Central Experiment Station.

[1] S. P. Kinney: The Blast-furnace Stock Column. U. S. Bur. Mines *Tech. Paper* 442 (1929).

[2] S. P. Kinney and C. C. Furnas: Gas-solid Contact in the Shaft of a 700-ton Blast Furnace. U. S. Bur. Mines, *Reports of Investigations*, Serial 2939 (1929).

[3] T. L. Joseph: Importance of Gas-solid Contact in the Blast Furnace. *Fuels and Furnaces* (1928) 635.

working to full capacity, which means uniform flow. Mechanical features, such as higher pressure drop and difficulty in settling, might interfere with operation, but in so far as such items do not interfere, uniform flow is the ideal condition.

Relation between Gas Flow and Particle Size

The course of the gas stream through the furnace depends primarily upon the distribution of the particles of different sizes throughout the column. A study has been made of the variables affecting gas flow under conditions of constant temperature,[4] and for materials comparable to blast-furnace materials it was found that the weight of gas flowing per second varies approximately as the 0.8 power of the diameter of the particle. However, in those sections of the blast furnace through which the gas flow is greater the temperature is also greater and the increased rate of flow is less than for isothermal conditions. Computations based on gas-temperature and gas-velocity data[5] have shown that for blast-furnace conditions the weight of gas flowing per second varies approximately as the 0.65 power of the particle size. The problem of obtaining uniform gas flow then resolves itself into the problem of obtaining uniform particle size distribution across the plane.

Study of the Fundamentals of Charging

The obvious angle of attacking the problem is to study the factors controlling size distribution. A properly conducted group of experiments should point out the fundamental factors that determine charging characteristics and should indicate the possibilities of control that are available to the furnace operator and to the designer.

Operating Compromises

If a blast furnace is to be economical it must operate rapidly and as a result the rate of driving is usually pushed to the limit. The operator is faced with the problem of working out the best charging methods that will permit reasonably rapid rates of blowing and uniform descent of stock. The lining must be preserved; production of dust must be minimized and provision made for the most efficient contact between the two phases, gas and solid. An investigation of the interior of several furnaces has shown such striking irregularities in gas distribution that the question naturally arises as to whether more uniform distribution can be secured without sacrificing other desirable operating features. Many operators are aware of the fact that there is much to hope for in the way of better gas distribution. It is generally appreciated that better prepara-

[4] C. C. Furnas: The Flow of Gases through Beds of Broken Solids. U. S. Bur. Mines *Bull.* 307 (1929).

[5] S. P. Kinney and C. C. Furnas: *Op. cit.*

tion of raw materials would greatly simplify the problem of gas distribution. The operator, however, also controls the gas distribution by methods of filling. The chief purpose of this investigation is to establish the trends in size distribution that result from various changes in filling. Preliminary treatment of raw materials, a more effective method of controlling gas distribution, is also discussed.

Experiments with Models

Naturally, the first impression about experiments with models is that they can show nothing of value or interest for a piece of equipment as large as the commercial furnace. Careful investigation, however, has convinced the authors that such is not the case and the model is very useful in displaying trends of operation; for instance, increasing the distance from the bell to the stock line has much the same effect as it has in a large furnace. Although there may not be a quantitative agreement between model experiments and practice, a great deal of valuable information may be obtained from the former.

Models are used extensively and successfully in the study of complicated physical problems, particularly in aerodynamics and in nautical work and the extrapolations necessary for application are much greater than those required in the present work.

Advantages and Disadvantages of Models

The obvious advantage in the use of models is reduction in size. If a blast furnace is used the material handled goes up as the third power of the linear dimensions; therefore, to conduct a charging experiment with a 17-ft. blast furnace requires the handling of 4913 times as much material as the same experiment scaled down for a model 1 ft. in diameter. Hence, the information can be obtained with the model much more quickly and economically. One man probably can do as much experimentation with a small blast-furnace model in one day as several men can in a month with the full-sized equipment.

With small equipment it is often possible to study particular items that could not possibly be studied in a large apparatus, as size usually adds complications.

The disadvantage in the use of models is that the results obtained may not be applicable to the large apparatus. Sometimes it is possible to make an accurate mathematical analysis of the problem and to show that model experiments are applicable to any desired size of apparatus.[6] The present study on charging furnaces is not susceptible to clear-cut analysis, but by making a few assumptions it can be shown that if the size of materials used in the model are scaled down in proportion to the

[6] E. Buckingham: Model Experiments and the Forms of Empirical Equations. *Trans.* Amer. Soc. Mech. Engr. (1915) **37.**

size of the equipment the results obtained in a model should be proportional to those for the large equipment.

As some assumptions were necessary in the mathematical treatment, one might expect that actual practice would not coincide with expectations. The results on models probably will not be in quantitative agreement with practice but there should be a qualitative agreement; that is, a factor such as bell clearance which affects a model in a given direction should affect a commercial furnace in the same direction. Confidence is added to the work by the fact that the models of different sizes (1 to 3 ft. dia.) give similar results and that these results agree with facts that are definitely known about charging characteristics of commercial furnaces.

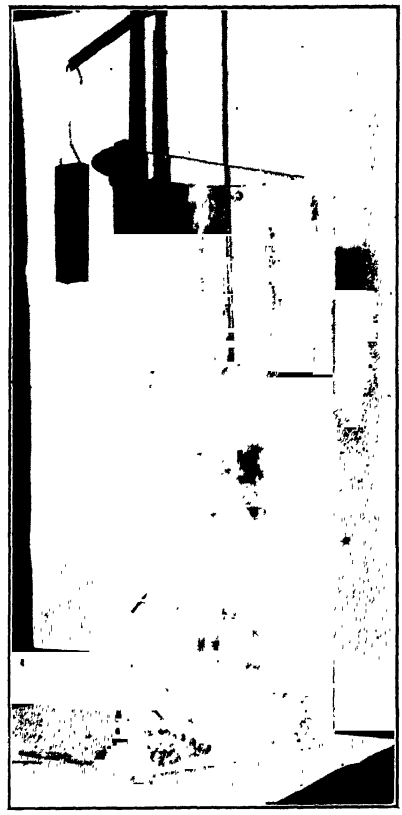


FIG. 1.—BLAST-FURNACE MODEL, 1 FT. DIAMETER.

DETERMINATION OF BEST METHOD OF FILLING

The ideal condition would be to have information so complete that one could predict that with a given furnace and given raw materials a given type of filling would give certain exact results, but that would be expecting too much of a mechanism as complicated as the blast furnace. If it is known, however, that a furnace is running with an undesirably open center it should be possible to manipulate the charging process so that the open center might at least be partly remedied. The best method of controlling furnace charging would seem to be first to determine the actual condition of the size distribution in the stock column by methods such as those developed by Kinney. It is a relatively simple matter to drive heavy iron tubes into the blast-furnace stock column and to determine the character of the gas flow by measurement of gas velocity, temperature, or gas composition.[7]

The second step would be to decide on a better distribution of size and the third, to change the method of charging to produce the desired results. The authors believe that the relation between changes in charg-

[7] S. P. Kinney: *Op. cit.*

ing and trends in size distribution, as shown by model experiments, can be applied in the last step.

The experiments with models dealt only with methods of charging, hence it was only necessary to design them to correspond to the top of the furnace where there is no batter. The models were half cylinders made of sheet metal with an open front which could be covered with glass. The

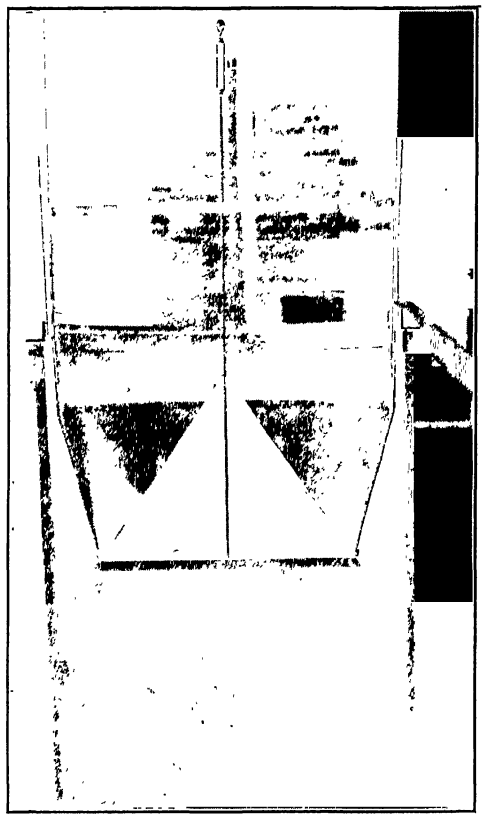


FIG. 2.—BLAST-FURNACE MODEL, 3 FT. DIAMETER.

big bell and hopper were also made in half sections. No little bell was used, and the materials were deposited directly into the hopper. The models having diameters of 1 ft. and 3 ft. are shown in Figs. 1 and 2. All parts are proportional in size to corresponding parts in the average commercial furnace. Unless otherwise designated, the bell clearance was proportional to 2 ft. of clearance in a furnace of 17 ft. dia. Each model has a false bottom built up by placing a charge of coke in the model and then setting it in place with plaster of Paris. This bottom gave a permanent and uniform stock line.

Materials and Operation

The materials used were iron, ore, and coke. Limestone was not studied, as it is one of the minor constituents of the charge and has little effect. The coke was crushed to a size proportional to that used in a commercial furnace. The ore could not be scaled down to a size proportional to commercial furnace diameters, as such an arrangement called for a large proportion of dust so fine that the adsorbed air film on the particles

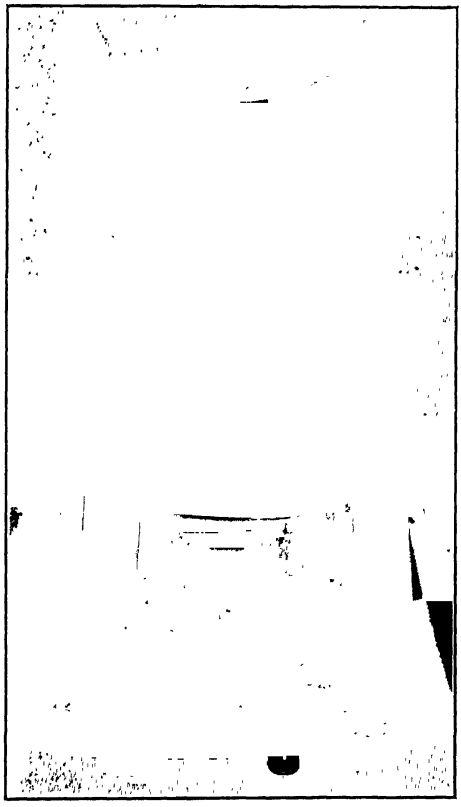


Fig. 3.—Furnace model with annular rings in place for sampling.

made the material behave abnormally. The ore finally used was obtained by screening out everything coarser than 6 mesh for the models of 12 to 15 in. dia. and everything larger than 3 mesh for the model 36 in. dia. The coke used was 2 to 4 mesh for the small models and 0.525 to 1.05 in. for the large model.

An experiment was usually made up of three rounds. A blank of coke was placed in the hopper and the bell lowered. Then the bell was closed and the hopper raised and fastened so that the distance to the top of the stock line was the same as that for the preceding round. A round of ore and coke was placed in the hopper and the big bell again

lowered. This procedure was repeated as often as desired. To obtain sections of the material after the experiment was completed, the charge was soaked with a fine spray of water, so that the material was not disturbed. Then concentric sections of the bed were taken out for screen analysis, by means of the metallic rings shown in Fig. 3.

The screen analyses were changed to a volume basis and the average particle size was computed. The average was not the arithmetical mean but the reciprocal mean; that is, the reciprocal of the sum of the reciprocals of the individual diameters each multiplied by the proportion present. The gas flow is determined by this reciprocal average rather than by the arithmetical average;[8] therefore it has considerably more significance for this work, as the gas flow is the item of primary importance. The data on average size are correlated with the radial distance from the center. Each annular ring is assumed to be uniform around the entire circumference. In studying the data one should remember that uniformity across the plane is probably what is desired.

Variables Studied

The factors studied with the small furnace models may be divided into two classes: (1) those of operation and (2) those that the operator cannot change but that are essential features of design. The following variables were studied:

Under the Control of the Operator

1. Distance from bell to stock line.
2. Order of charging.
3. Size of charge.
4. Splitting the charge.
5. Mixing the charge.
6. Wetting the charge.

Essentially Features of Design

1. Bell angle.
2. Bell clearance.
3. Distance the bell drops.

Height of Stock Line

In general, the greater the distance from the bell to the stock line, the greater the disparity between particle size at the center and at the wall. The results of a series of experiments on the 1-ft. model are plotted in Fig. 4. The higher the bell is above the stock line, the greater is the particle size at the center. Data on computed particle size for a commercial furnace[9] are also given on a comparative scale in this figure. The curve corresponds closely to the curve of particle size in the model when the bell was 9 in. above the bed. This close agreement adds considerably to the confidence that may be placed in the experiments

[8] C. C. Furnas: *Op. cit.*, "Use of Reciprocal Averages."
[9] S. P. Kinney and C. C. Furnas: *Op. cit.*

with models. A photograph of the cross-section of the bed for the run in which the bell was 9 in. above the bed is given as Fig. 5. Similar results were obtained with the 3-ft. model, and are plotted in Fig. 6. With the larger as with the smaller model, the greater the distance between the bell and the stock line, the greater the disparity in particle size between the wall and the center.

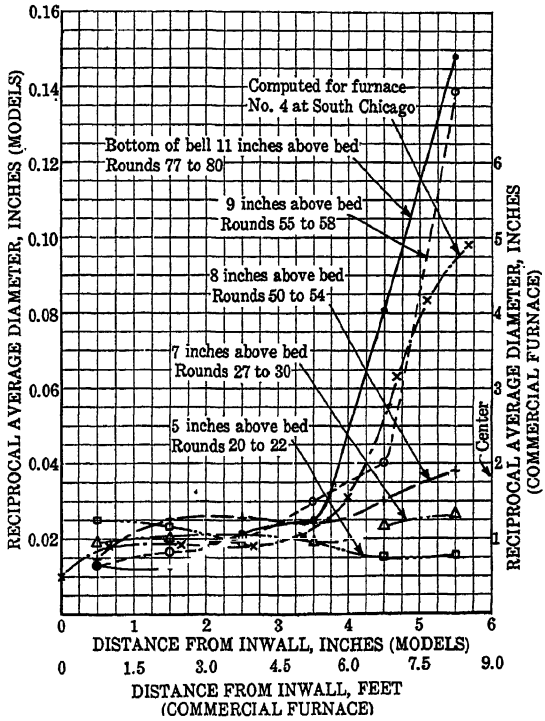


FIG. 4.—AVERAGE PARTICLE SIZE IN SMALL BLAST-FURNACE MODEL FOR DIFFERENT HEIGHTS ABOVE BED. COMPARISON WITH COMPUTED SIZE IN ONE COMMERCIAL FURNACE.

Order of Charging

The charging characteristics depend considerably upon the order of placing the materials in the hopper. When ore and coke are charged together the average particle size at the center is considerably larger if the coke is placed on the big bell first. The results of the experiments are shown in Figs. 7 and 8 for the two models. An idea of the actual appearance of the bed can be obtained from Figs. 9 to 12. Fig. 9 shows normal charging (ore on the big bell first) in the 1-ft. model. Fig. 10 is the same model with coke on first. One can easily see that the charge is much more open at the center in the case of reversed charging (coke on the big bell first). Figs. 11 and 12 show the same orders of charging for the 3-ft. model.

FIG. 5.—TYPICAL CHARGING EXPERIMENT.
Model 1 ft. dia.; hopper 9 in. above bed; bell drop 1¼ inches.

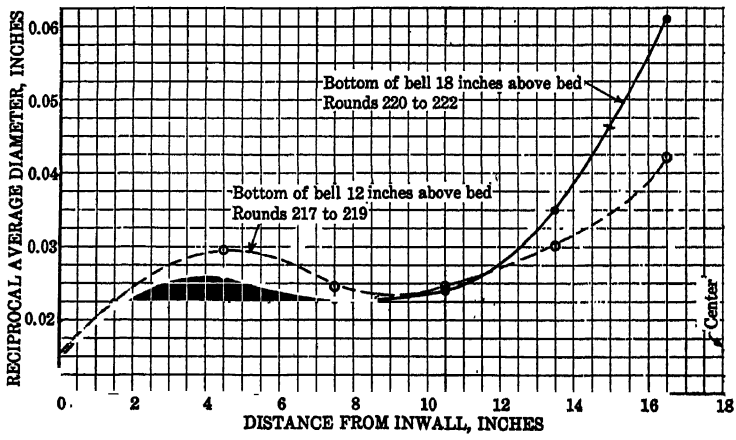


FIG. 6.—AVERAGE PARTICLE SIZE IN LARGE BLAST-FURNACE MODEL FOR DIFFERENT HEIGHTS ABOVE BED. BELL DROP 4 INCHES.

Size of Charge

Up to a certain limit, the smaller the size of the charge, the greater the discrepancy in particle size between wall and center. The results of experiments on varying size of charge are shown in Fig. 13. The full charge corresponds to approximately 30,750 lb. of ore and coke in a furnace with a stock line 17 ft. dia. When the size of the charge was halved the average particle size at the center increased by about 35 per cent. Increasing the charge to three times normal size made no material

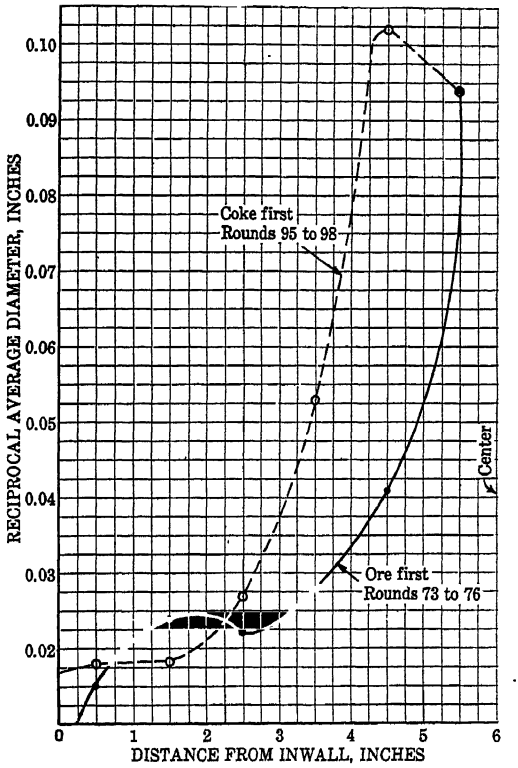


FIG. 7.—EFFECT OF CHANGING ORDER OF CHARGING.
Model 1 ft. dia.; hopper 10 in. above bed; bell drop 1¼ inches.

difference in the distribution of particle size. Apparently a round of 30,000 lb. is about the most advantageous for furnace practice.

Splitting the Charge

A round of ore and coke is often split and each constituent charged separately. The results of experiments on this method of charging for both models are given in Figs. 14 and 15. The model experiments show little difference between normal charging (ore and coke charged together, ore on the big bell first) and split charging (ore and coke charged

separately). There might be some difference in a large furnace, but it would probably not be large.

Mixing the Charge

Mixing the constituents of the charge apparently has a very serious effect on distribution of particle size. In experiments with the 1-ft. model the particle size at the center increased 300 per cent. when the ore and coke were mixed. The results of the experiments are shown in Fig. 16.

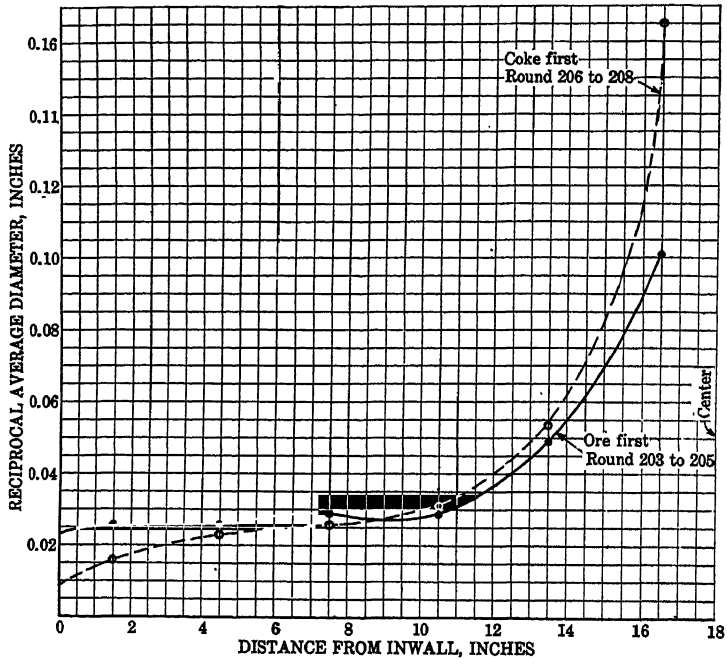


FIG. 8.—EFFECT OF CHANGING ORDER OF CHARGING.
Large model 3 ft. dia.; hopper 15 in. above bed; bell drop 4 inches.

Wetting the Charge

The effect of wetting the charge is difficult to determine. The 3-ft. model was used for this study. The charging characteristics are usually the same whether the ore is relatively dry or very wet, but when just enough water is present in the ore to give it a doughlike consistency the charging characteristics become undesirable. The results of experiments on the effect of the moisture content of the ore are shown in Fig. 17. The curves of particle size for air dry, for 7.1 per cent. water and for 18 per cent. water are practically the same. With 12.5 per cent. of water the ore was like stiff mortar and, although the average particle size at the exact center was small, there was an annular ring one-third of the way from the

center to the wall in which the average particle size was large and the cross-sectional volume large also and hence undesirable. It would seem best to charge the ore either relatively dry or very wet.

Bell Angle

Bells with an angle of 45° and 55° were used in the 3-ft. model. The steeper bell gave the better charging characteristics; that is, less disparity between particle size at the wall and at the center. The results of the experiments are shown in Fig. 18.

FIG. 9.—DISTRIBUTION WITH NORMAL CHARGING, SMALL MODEL.

FIG. 10.—DISTRIBUTION WITH REVERSED CHARGING, SMALL MODEL.

Bell Clearance

Bell clearance is of considerable interest to furnace designers. The normal bell clearance is usually about 2 ft. for a furnace with a stock line 17 ft. dia. A series of experiments was made with the bell hopper of the 1-ft. model, using cylinders of different sizes to attain the bell clearance. The largest bell clearance used was 207 per cent. of the normal; that is, it corresponded to a clearance of slightly more than 4 ft. in a furnace with a 17-ft. stock line. This study was complicated by the marked change in the effect of bell clearance with change in the distance from the big bell to the stock line. Generally, the greater the bell clearance the more

nearly uniform the particle size across the plane. but the effect increases as the stock line becomes shorter.

The results of a series of experiments for different heights of the bell above the bed are shown in Figs. 19, 20, and 21. The increase in particle

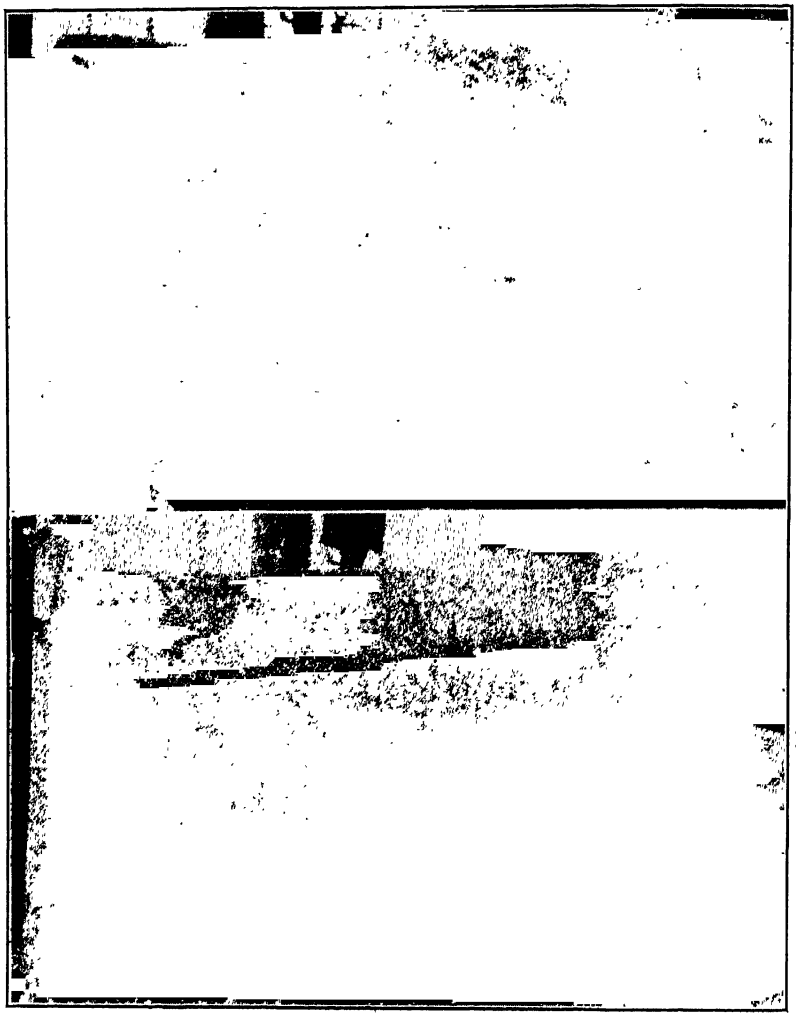


FIG. 11.—DISTRIBUTION WITH NORMAL CHARGING, LARGE MODEL.
FIG. 12.—DISTRIBUTION WITH REVERSED CHARGING, LARGE MODEL.

size at the wall is apparently very small with increase in bell clearance but is nevertheless significant. To give an idea of the relative change in distribution of particle size, the percentage changes of diameter compared to normal clearance are plotted in Figs. 22, 23, and 24, for the different bell clearances and heights of stock line. The relative effect is marked.

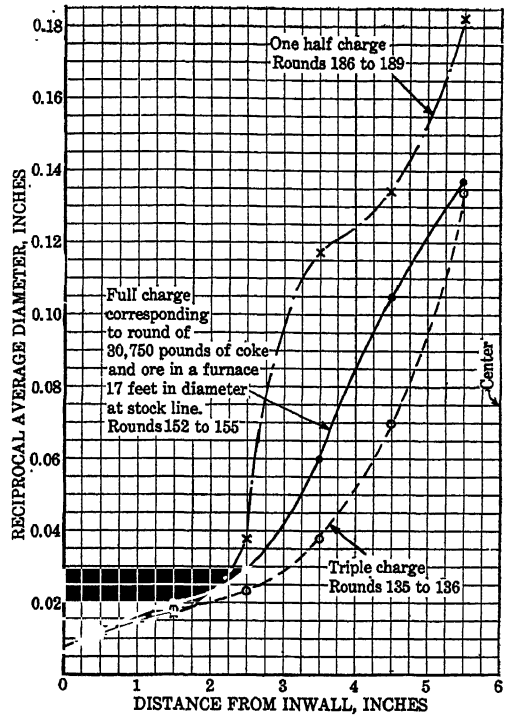


FIG. 13.—EFFECT OF VARYING SIZE OF CHARGE.

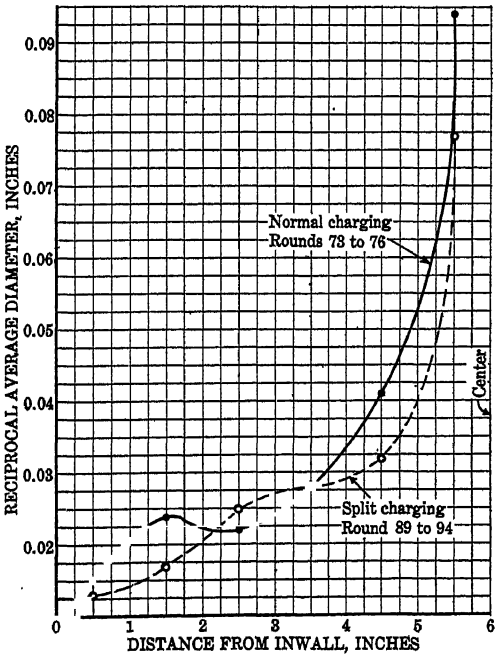


FIG. 14.—EFFECT OF SPLITTING CHARGES (COKE AND ORE CHARGED SEPARATELY) FOR 1-FT. MODEL.

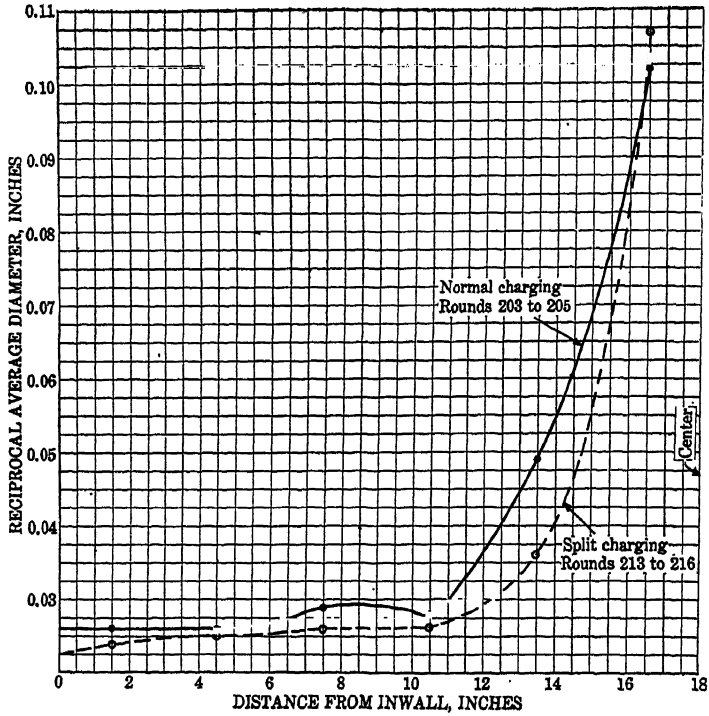


FIG. 15.—EFFECT OF SPLITTING CHARGES (COKE AND ORE CHARGED SEPARATELY) FOR 3-FT. MODEL.

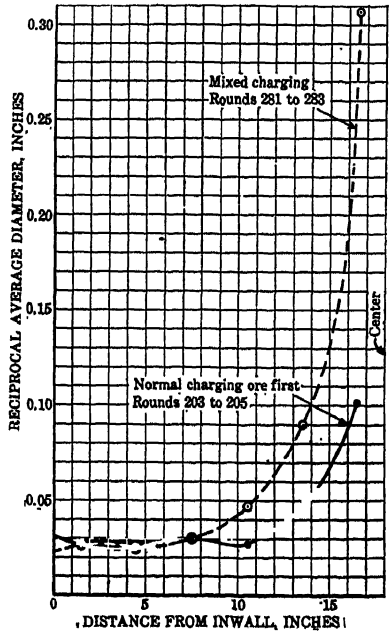


FIG. 16.—EFFECT OF MIXING ORE AND COKE, ON DISTRIBUTION OF PARTICLE SIZE.

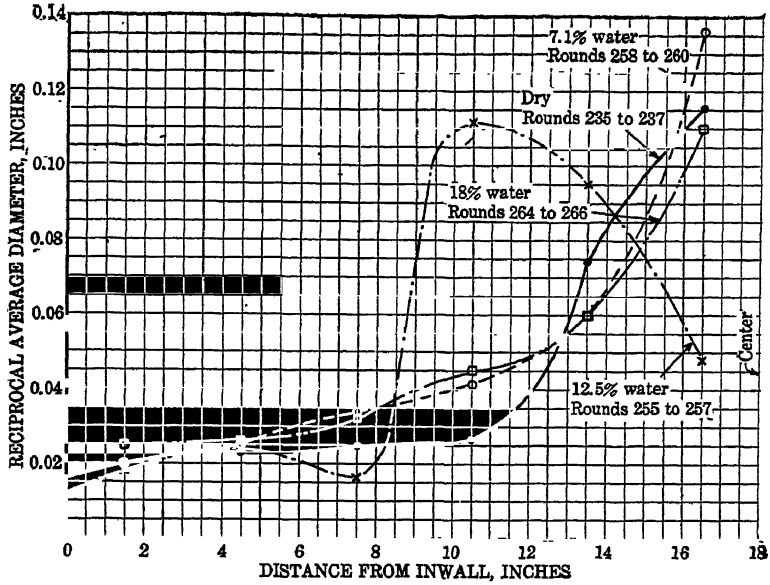


FIG. 17.—EFFECT OF MOISTURE CONTENT OF ORE; 3-FT. MODEL, 45° BELL.

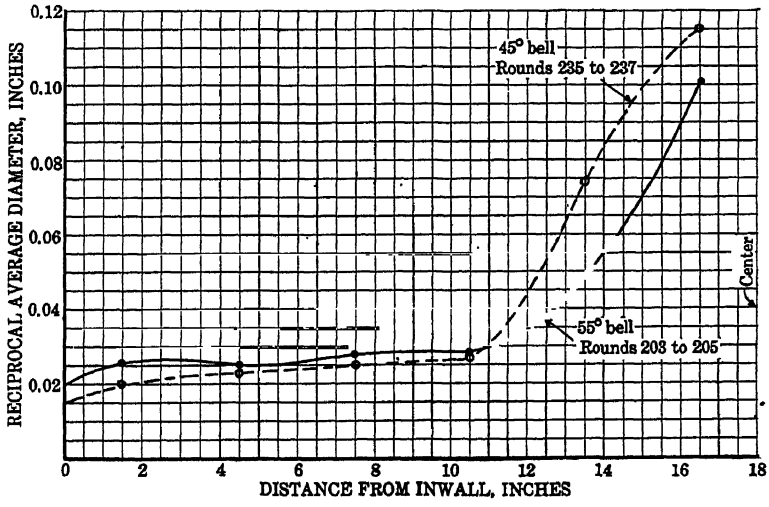


FIG. 18.—EFFECT OF BELL ANGLE ON DISTRIBUTION OF PARTICLE SIZE.
Model 3 ft. dia.; bottom of hopper 15 in. above bed; bell drop 4 inches.

Length of Bell Drop

The greater the distance the bell drops, the less the disparity in particle size between the wall and the center. The results of three sets of experiments on the 1-ft. model are shown in Fig. 25.

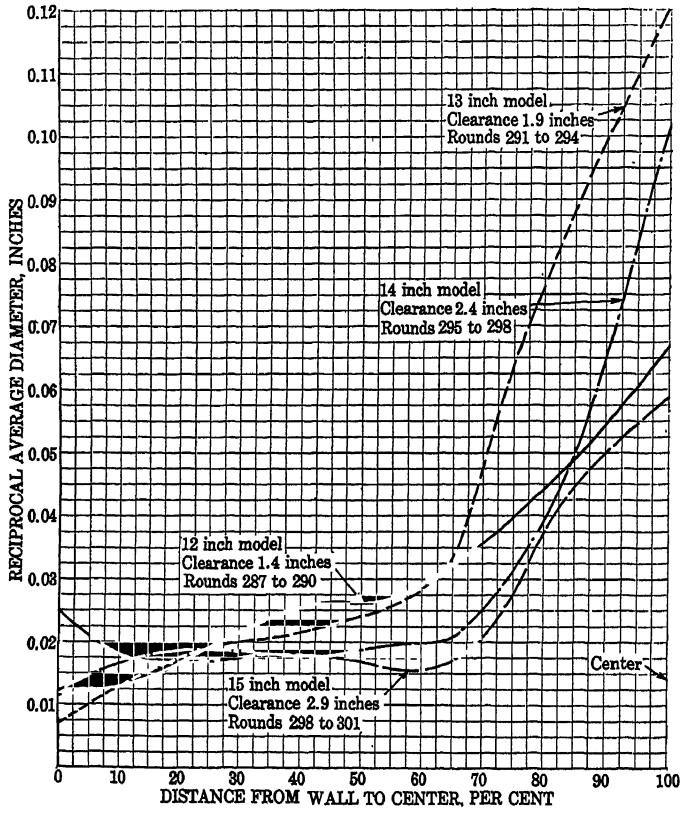


FIG. 19.—RELATION BETWEEN BELL CLEARANCE AND SIZE DISTRIBUTION IN CHARGE. Hopper 10 in. above bed. Bell clearance of model 12 in. dia. corresponds to clearance of 2 ft. in furnace with 17-ft. stock line.

GENERAL PRINCIPLES OF CHARGING

The principles underlying the charging characteristics of a furnace as shown by the foregoing experiments with models may be summarized in three simple statements:

1. The average particle size tends to be large at the center and small at the wall.

2. The more quickly the material is deposited on the stock line, the less the disparity in the size at the center and at the wall.

3. Increasing the bell clearance tends to open up the wall and to close up the center of the stock column.

The detailed mechanism of changing the character of the stock column may be summarized as follows:

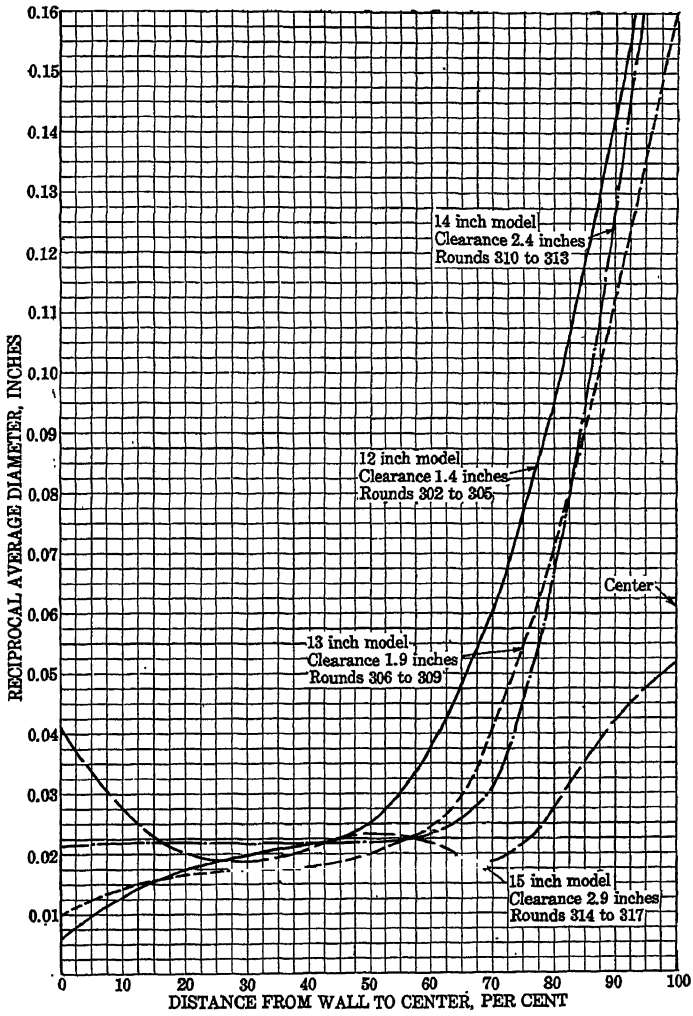


FIG. 20.—RELATION BETWEEN BELL CLEARANCE AND SIZE DISTRIBUTION IN THE CHARGE. Hopper 8 in. above bed. Bell clearance in 12-in. model corresponds to clearance of 2 ft. in furnace with a 17-ft. stock line.

1. The average particle size at the center can be diminished by:

   a. Keeping the stock line close to the bell.
   b. Increasing bell angle.
   c. Increasing distance and speed of bell drop.
   d. Increasing bell clearance.

2. The average particle size at the center can be increased by:

a. Reversing items *a*, *b*, *c*, or *d* under 1.
b. Charging the coke on to the big bell before the ore.
c. Diminishing the size of round.
d. Mixing the ore and coke before charging.

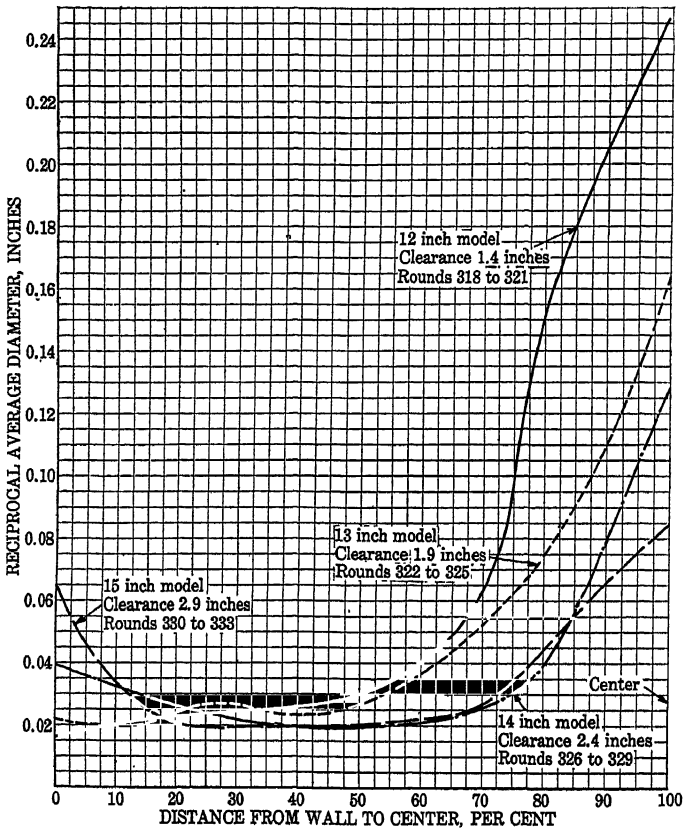


FIG. 21.—EFFECT OF BELL CLEARANCE ON SIZE OF PARTICLES IN BED.
Hopper 6 in. above bed. Bell clearance in 12-in. model corresponds to clearance of 2 ft. in furnace with a 17-ft. stock line.

VARIETY OF METHODS

Thus, several means to accomplish the same results are available. For example, increasing bell clearance decreases particle size at the center and increases it at the wall; but the particle size can be changed in the same direction by keeping the stock line close to the bell, increasing the bell angle, or increasing the speed and distance of bell drop.

VARIABILITY OF FURNACES

Although furnaces built with the usual American lines might be expected to operate with an open center and dense periphery, some

furnaces in which the opposite was true have been investigated. This difference in operation may be caused by wider hearth, by greater batter, or by rapid blowing. In such instances, it would be desirable to open up the center and, as indicated above, this might be accomplished in a number of ways.

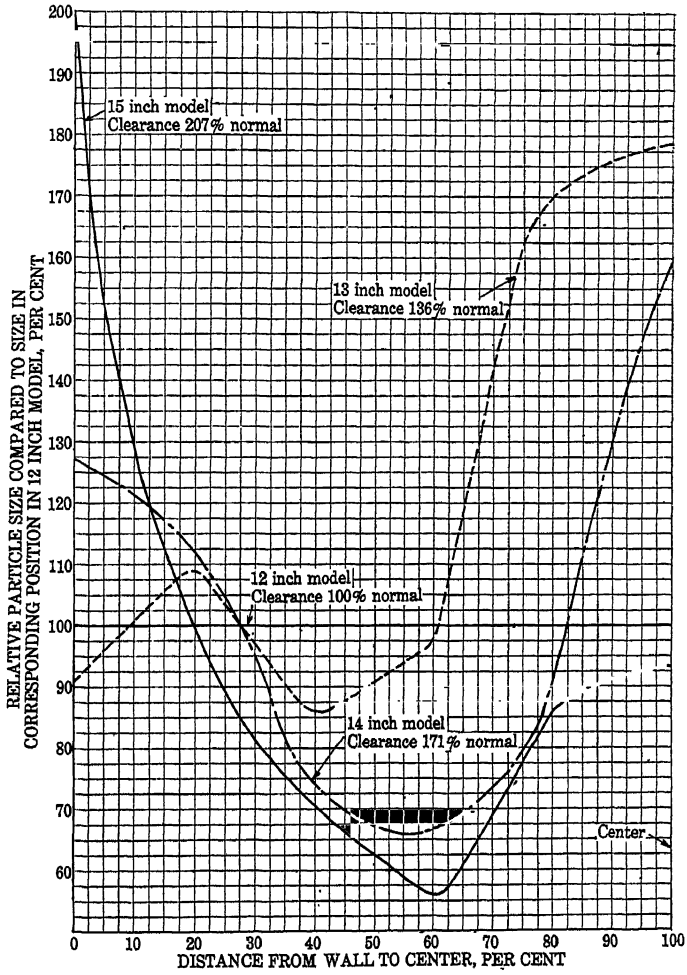


FIG. 22.—RELATIVE DISTRIBUTION OF PARTICLE SIZE FOR DIFFERENT BELL CLEARANCES. Hopper 10 in. above bed. Bell clearance of 100 per cent. corresponds to 2 ft. of clearance with a stock-line diameter of 17 feet.

NECESSITY FOR FURNACE SURVEYS

As pointed out, a determination of actual gas distribution is the first logical step in seeking better gas distribution. If the gas flow across the furnace is investigated either by a study of temperature conditions,

gas composition, gas velocity, or all three,[10] then steps may be taken to correct whatever undesirable conditions may exist. The authors believe that the foregoing experiments on the models should prove valuable in indicating the type of change that should be made in the mechanism of charging to produce a desired result in the stock column.

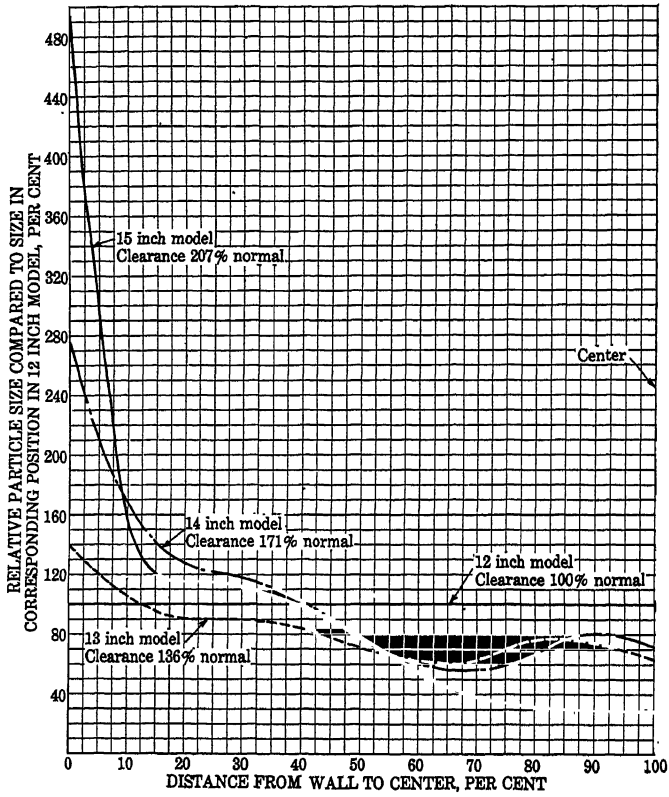


FIG. 23.—RELATIVE DISTRIBUTION OF PARTICLE SIZE FOR DIFFERENT BELL CLEARANCES. Hopper 8 in. above bed. Bell clearance of 100 per cent corresponds to 2 ft. of clearance with a stock line of 17 feet.

ORE TREATMENT

So far this paper has dealt with means of introducing given materials into the furnace. There are also a great many ways of treating the materials before they enter the process.

FLUE DUST

One of the most undesirable features of furnace operation is the production of the flue dust. Investigation of a series of screen analyses of dust from commercial furnaces and of samples from laboratory dusting

[10] For methods of making such a survey, see S. P. Kinney: *Op. cit.*

experiments indicates that practically all of the flue dust is made up of material finer than 14-mesh. The question arises: What proportion of this potential flue dust is actually blown out in the operation of a furnace?

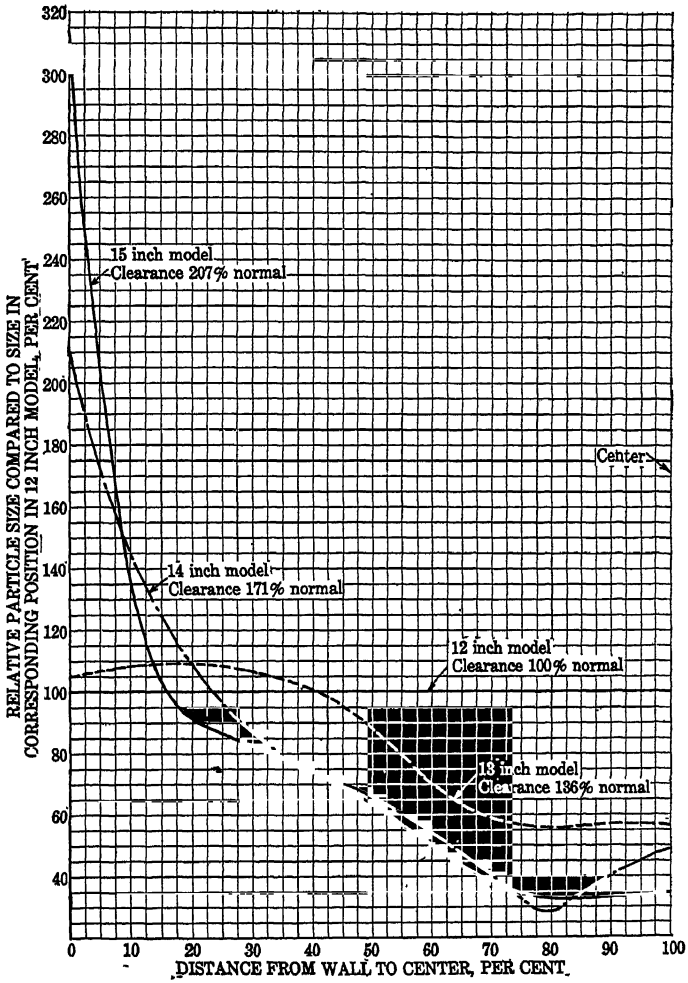


FIG. 24.—RELATIVE PARTICLE SIZE FOR DIFFERENT BELL CLEARANCES.
Hopper 6 in. above bed. Bell clearance of 100 per cent. corresponds to 2 ft. of clearance with a stock-line diameter of 17 feet.

Experiments on Dusting

A series of laboratory experiments were made with a gas stream that had approximately the same lifting power as the gas stream in a blast furnace. Relatively little potential flue dust was actually blown out in the process. The results are plotted in Fig. 26, which shows that the proportion of flue dust blown out increases progressively as the amount of fines in the bed increases. Two points from the operation of commercial

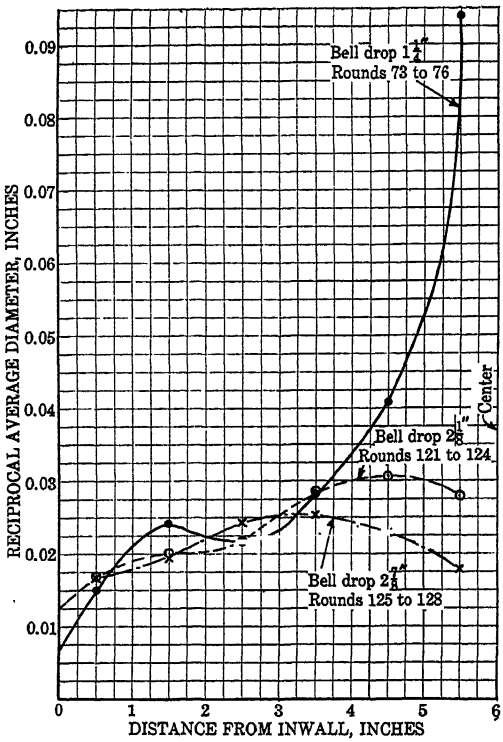


FIG. 25.—AVERAGE PARTICLE SIZE IN 1-FT. MODEL FOR DIFFERENT BELL DROPS.

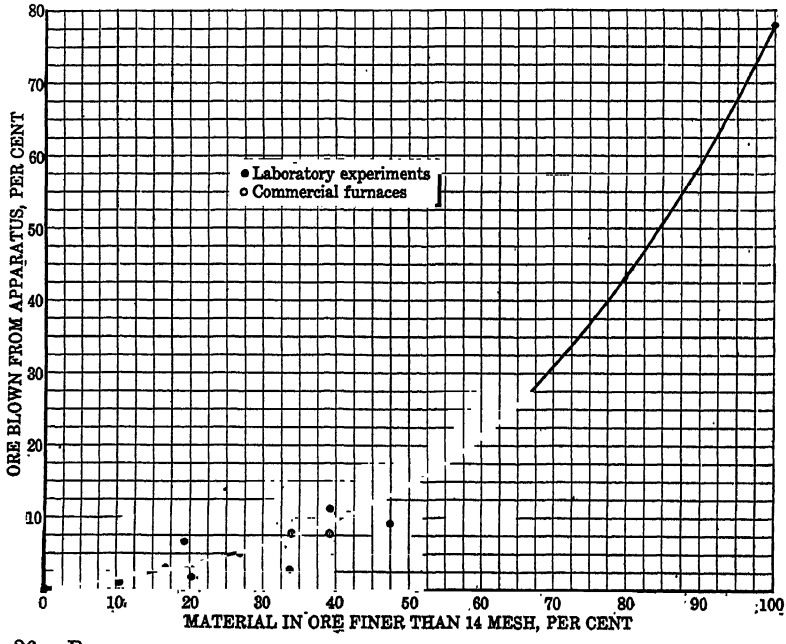


FIG. 26.—RELATION BETWEEN FINE MATERIAL IN CHARGE AND AMOUNT BLOWN OUT

furnaces are included in the graph. One can see that they coincide well with the experimental curve.

Although dust production can be aided by proper distribution of the stock in the furnace, some dust will always be produced as long as the charge contains material finer than 14 mesh. The dust that is blown out of a furnace is usually sintered and charged again. Sintering the potential flue dust before it is put into the furnace, thus eliminating the handling of the material and a great deal of the gas cleaning, would seem more logical.

Advantages of Sintering

Sintering a portion of the fine part of the ore before charging it into the furnace has other distinct advantages besides diminishing the amount of dust: (1) It tends to make the raw materials of more uniform size, which makes for more efficient and uniform operation of the furnace; and (2) it makes the size composition of the charge such that it should be possible to practice sizing with Lake ores, a practice that has distinct advantages, as will be pointed out later.

Sintering is of great interest at present but in this country, so far as the authors know, no large-scale operation has been attempted on the raw materials now in use. Probably sintering has not been undertaken generally because operators are doubtful as to the economy of the process.

Manipulation of Materials

The cost of sintering may be cut greatly by judicious manipulation of the raw materials. The screen analyses of typical samples of a group of common Lake ores are given in Table 1.

If fine material is to be obtained for sintering, the ore must be washed. The coarsest material that can be washed out of an ore conveniently is about 65 mesh. It would seem most practicable to take an ore containing a small amount of the fine material and to use that portion unsintered. For the rest of the charge it would be advisable to take an ore containing a large portion of fines, wash out the −65-mesh material, sinter it, and use the charge of mixed ores. Such a combination might be made of 50 per cent. of the group 3 Mesabi ore (column 1, Table 1), which contains only 6.6 per cent. of −65-mesh material, and 50 per. cent of Mahoning ore (column 7), which contains 28.2 per cent. of −65-mesh material. The Mahoning ore might be classed as a dust producer, but if the −65-mesh material is sintered the dust production, as indicated by Fig. 26, should be decreased markedly and would probably only be one-fifth to one-tenth of the original figure. Numerous desirable combinations of ores for sintering might be made in this way.

TABLE 1.—*Screen Analyses of Representative Samples of Some Ores Used in American Blast Furnaces*

Screen Size	1 Group 3, Mesabi, Per Cent.	2 Group 7, Mesabi, Per Cent.	3 Penoid Cadiz, Per Cent.	4 Wellington, Group 3, Per Cent.	5 Spruce, Group 4, Per Cent.	6 Leonidas No. 1 Shaft, Group Dirven, Per Cent.	7 Mahoning, Per Cent.	8 Bennett, Per Cent.	9 Croft Bessemer, Per Cent.	10 Melrose, Per Cent.	11 Zenith, Per Cent.	12 Cuyuna, Per Cent.	13 Vermillion, Per Cent.	14 Provo, Utah, Per Cent.
Inch														
+1.05	14.2	10.3	14.4	5.8	9.3	8.5	7.6	12.0	18.4	13.1	2.5	19.8	7.4	34.6
−1.05 +0.525	11.6	13.0	13.2	15.2	8.3	11.6	8.8	17.3	13.4	9.0	13.4	22.8	26.0	14.1
−0.525 +3 mesh	15.2	17.4	15.7	18.3	13.4	14.7	10.4	15.5	12.9	13.2	18.8	18.1	20.4	22.5
Mesh														
−3 +6	10.1	9.1	9.4	10.0	10.7	11.6	7.5	10.0	10.4	11.9	14.6	16.2	19.5	6.6
−6 +10	11.4	10.1	7.6	7.7	9.6	9.6	5.7	6.8	8.3	13.1	15.6	7.0	8.5	5.9
−10 +20	10.5	10.1	7.7	5.6	9.4	9.5	5.7	6.5	7.6	13.1	11.6	4.8	5.5	4.0
−20 +35	14.5	11.5	7.9	9.2	11.1	10.4	12.1	8.7	11.3	11.0	7.6	3.7	3.5	3.9
−35 +65	5.9	7.3	4.6	8.9	11.0	8.4	14.0	7.6	4.0	6.4	4.8	2.2	2.9	1.5
−65 +150	3.2	5.5	5.2	9.6	8.8	8.0	12.1	7.5	10.1	4.9	4.6	1.8	1.8	(−65 mesh)
−150	3.4	5.7	14.2	9.7	8.4	7.7	16.1	8.1	3.6	4.3	6.5	3.6	4.5	6.9

Economy

The benefits of sintering are decreased fuel consumption, more uniform operation of the furnace, a more uniform product, and a marked decrease in dust production. Reliable data on the possible savings for American practice are scanty, but available figures indicate that the process of sintering part of the fines of the charge is economically feasible.

Crushing

Very large pieces of ore are detrimental to furnace operation because of the slow rate of reduction in the interior of a large particle. The object of treating the ore is to bring all particles to as nearly uniform a size as possible; therefore oversize pieces should be crushed just as undersize pieces should be sintered. In some plants ore is now being crushed. Usually it is found advantageous to crush all ore to pass a 2-in. screen.[11]

Sizing

If each layer of material put into the furnace is of uniform size within itself, there should be little disparity in particle size between the wall and the center. Consequently, it would appear advantageous to separate the ore into different sizes and to charge each size separately.

The possibilities of sizing have probably been brought to operators' attention at various times in past years, but as far as is known the first systematic study of the subject was made by the U. S. Bureau of Mines.[12] Following the suggestion of sizing made in this paper, the Columbia Steel Corpn. of Provo, Utah, is now crushing all ore to pass a 2-in. screen, dividing the ore into three sizes and charging each size separately. The finest size is $-\frac{1}{2}$ in. and makes up 50 per cent. of the total charge. The change from standard practice to the practice of sizing has meant a fuel saving at Provo of approximately 20 per cent.[13]

One could not expect sizing to be advantageous on Lake ores as long as they contain such a large per cent. of fine materials; but, if a portion of the -65-mesh material were sintered into cakes, 50 per cent. of the ore would be coarser than 2 or 3 mesh and sizing would be possible. This is another distinct advantage of sintering.

It is much more advantageous to sinter the material into a cake than to nodulize it in a rotary kiln. The nodulizing process makes the material large enough so that it will not be blown out of the furnace but too small to increase the average size of particle in the bed appreciably,

[11] For instance, J. P. Dovel: Dovel-type Furnace Put on Test. *Blast Furnace and Steel Plant* (1928) **16**, 1555.

[12] P. H. Royster, T. L. Joseph and S. P. Kinney: Influence of Ore Size on Reduction. *Blast Furnace and Steel Plant* (1924) **12**, 274.

[13] S. P. Kinney: Effect of Sized Ores on Economy of Blast-furnace Operation as Based on Results of a 500-ton Furnace. U. S. Bur. Mines *Tech. Paper* 459 (in press).

whereas a sinter cake is large enough to be of material aid in increasing the average size of the ore particle.

Summary

1. For a blast furnace to operate efficiently there must be efficient contact between the gas stream and the solid particles. This implies uniform distribution of particle size from the inwall to the center.

2. Commercial furnaces show a great disparity in particle size between the center and the wall.

3. Experiments with blast-furnace models indicate that the uniformity of the stock column can be controlled partly by the methods of charging.

4. The average particle size at the center of a furnace may be diminished by:

a. Keeping the stock line close to the bell.
b. Increasing bell angle.
c. Increasing distance and speed of bell drop.
d. Increasing bell clearance.

5. The average particle size at the center may be increased by:

a. Reversing items *a*, *b*, *c*, or *d*, under 4.
b. Charging the coke on to the big bell before the ore.
c. Diminishing the size of the round.
d. Mixing the ore and coke before charging.

6. Most furnaces operate with an open center but exceptions have been found. The actual condition of the interior of a furnace should be determined before attempting to remedy conditions by manipulation of charging operations.

7. Treatment of the ore should prove advantageous in obtaining uniform particle size. Pieces over 2 in. should be crushed and the −65-mesh material should be sintered into a cake.

8. It has been found advantageous to divide ore into three different sizes and to charge each size separately.

DISCUSSION

A. G. McKee, Cleveland, O.—This is a subject which has been of great interest to me for many years, and with the meager information available, I have studied it as accurately as I could, but this paper and the other work that has been done by Mr. Joseph, and his associates, gives us a new key to the solution of many of the problems which have confronted us all these years. In fact, the work that has been done by Mr. Joseph and his associates during the past few years is most valuable, and I believe that it is the one big contribution to the art of smelting iron ore that has come to the blast-furnace men since the work done by Sir Lowthian Bell, years ago.

The information that we have received indicates clearly the desirability of tops of larger diameter in the furnaces we are building, and of a somewhat smaller bell in proportion to that size. As a further means for control of radial distribution there are also the use of a steeper bell, a quicker movement of the bell, and somewhat greater travel. All of these things, when fully understood as the result of further study and

intelligent trial on a large number of furnaces will be of great value in improving the operation of the furnace, decreasing the amount of flue dust produced, and making for a more efficient smelting due to a more uniform travel of the gas through all of the ore in the top of the furnace.

Keeping the stock more closely filled up to the bell is another point that has been talked about and often neglected. Many years ago I was walking through the Edgar Thompson blast-furnace plant with old Mike Killeen, when he saw one of the furnaces slipping badly. He upbraided his men and his complaint was that they were not keeping the furnace full, they were letting it get too far down, and it was slipping accordingly. The figures accompanying this paper indicate just why that was. In other words, by allowing the furnace to run with the stock too low, there was too much ore against the furnace wall and too much coke in the middle, and the furnace was accordingly slipping and working badly. These things, which up to the present time have been matters of guesswork, will be possible of much more accurate solution because of this information, and I would suggest a more intimate study of this paper and the other information given out by the Bureau of Mines by all blast-furnace men. If it is correctly interpreted and intelligently applied to our blast furnace problems, I am sure that the industry will be materially helped by this work.

C. C. FURNAS.—It is very gratifying to know that our laboratory results are borne out in practice. This is particularly true when it is realized that when volume is considered the smallest model used was about one five-thousandth as large as a commercial furnace and the largest model about one two-hundredth as large.

Although it was spoken of in the paper, it might be well to mention again that the laboratory results should be considered with some reservation. The authors wish to emphasize that the experiments with models probably give reliable information only as to trends and that it would hardly be justifiable to carry the quantitative data bodily over into furnace practice. For example, Figs. 19 to 24 show that increasing the bell clearance in the models opens up the wall and closes up the center of the stock column. In all probability this is true in commercial furnaces. However, in Fig. 24 the increase in particle size at the wall was only 5 per cent. for an increased bell clearance of 36 per cent. Translated into blast-furnace dimensions this would mean that a furnace 17 ft. in dia. at the throat with a 13-ft. bell would be increased to almost 18½ ft. in dia. if the bell-size remained the same. It is very likely that this increase of 1½ ft. in the dia. of the stock line would cause more than a 5 per cent. increase in particle size at the wall. The laboratory work is still valuable, however, in showing the trend which may be expected.

It can not be too strongly emphasized that investigation of the gas-flow conditions in furnaces should be very valuable to the operators. Such an investigation is very inexpensive and a relatively simple matter in the upper, cooler parts of the furnace. The method of doing this was indicated on page 99. The only personnel required is a technical man who understands the significance of thermocouples and of gas samples and gas velocities, and the occasional services of three or four laborers. It is hardly too much to expect that in the future frequent investigation of the gas flow conditions in the upper part of the furnace will be part of the routine operation.

The authors hope that the material in the present paper may be of some small aid in solving some of the perplexing problems of design and operation of furnaces.

Effect of Barium Oxide on the Desulfurizing Power of Blast-furnace Slags*

By C. E. Wood† and T. L. Joseph,‡ Minneapolis, Minn.

(New York Meeting, February, 1929)

This paper is a brief report of experimental work undertaken to determine whether barium oxide in any quantity increases the desulfurizing action of blast-furnace slags. Industrial furnace operation with slag containing small quantities of barium oxide, referred to later, interested S. A. Sanford of the Commercial Chemical Co., Youngstown, Ohio, to conduct experiments to furnish comparative results on desulfurization with normal slag and slag containing small quantities of barium oxide. The U. S. Bureau of Mines agreed to assist on the problem because of the possible saving in fuel if the desulfurizing action of blast-furnace slag can be substantially increased, also because the experiments would yield new information on sulfur elimination in general, a matter of economic importance in furnace practice. A more complete and fundamental study of desulfurization of iron by slag is in progress.

Distribution of Sulfur in the Blast Furnace

More than 90 per cent. of the total sulfur entering the blast furnace is in the coke. Sponge iron formed by reduction of iron oxides absorbs part of the sulfur as ferrous sulfide. Kinney's examination of samples,[1] taken from various levels of a 300-ton furnace, shows that the metal continues to take up sulfur until it reaches a level near the tuyeres. Desulfurization must therefore take place as the metal falls through the slag and as the slag and metal exist as layers in the crucible.

The relative amounts of sulfur removed while the metal falls through the slag and while the slag and metal exist as layers in the crucible are not definitely known. Preliminary experiments by the

---

* Published by permission of the Director, U. S. Bureau of Mines.

† Assistant Chemist, North Central Experiment Station, U. S. Bureau of Mines.

‡ Supervising Engineer, North Central Experiment Station, U. S. Bureau of Mines.

[1] S. P. Kinney: Composition of Materials from Various Elevations in an Iron Blast Furnace: U. S. Bur. Mines *Tech. Paper* 397 (1926) 6.

writers[2] indicated that both methods of removing sulfur should be investigated in comparing the rates of sulfur absorption by various slags.

Qualitative information on the desulfurization which can be accomplished by various slags is available from blast-furnace practice. For example, it is generally accepted that the most basic slag that can be handled in the furnace and the highest hearth temperatures give the best desulfurization. Herty and Gaines[3] have shown the effect of temperature and percentage of FeO in the slag on the amount of sulfur in the metal. Johnson,[4] in his discussion of the blast-furnace process, mentioned the importance of data showing the rate of sulfur absorption by slags of various composition when subject to the same conditions; he also pointed out that such information was not available. In a study of the reactions in the blast furnace the effect of viscosity and composition of the slag have been discussed by Feild and Royster[5] and Royster and Joseph.[6]

Barium Oxide in Furnace Slag

Sweetser[7] has reported some experience in operating a blast furnace on slag containing about 2.5 per cent. barium oxide. In this connection he stated:

> When the silica in a blast-furnace slag goes below 30 per cent. and the sum of the silica and alumina is below 43 per cent., there is danger of a "lime set" in the furnace, or at least some very low silicon iron, and usually the composition of the slag should be changed at once. Such slags are nearly always hard to manage both inside and outside the furnace, and are so refractory that they require too much coke per ton of pig iron for economical practice. But when a slag with such an analysis is found to be fluid and easy running, and the coke per ton of pig is exceptionally low, there is need for further investigation of the slag.

A complete analysis of the slag gave 0.40 per cent. FeO, 29.15 per cent. SiO_2, 13.40 per cent. Al_2O_3, 45.10 per cent. CaO, 5.10 per cent. MgO, 2.45 per cent. BaO, and 1.85 per cent. S.

---

[2] T. L. Joseph, S. P. Kinney, and C. E. Wood: Production of High-alumina Slags in the Blast Furnace. Iron and Steel Technology in 1928 (A. I. M. E.) 82.; U. S. Bur. Mines *Tech. Paper* 425 (1928) 26.

[3] C. H. Herty, Jr. and J. M. Gaines, Jr.: Desulphurizing in the Blast Furnace. *Blast Furnace and Steel Plant* (1928) **16**, 234.

[4] J. E. Johnson, Jr.: Principles, Operation, and Products of the Blast Furnace. 1918. McGraw-Hill Book Co., Inc.

[5] A. L. Feild, and P. H. Royster: Slag Viscosity Tables for Blast-furnace Work. U. S. Bur. Mines *Tech. Paper* 187 (1918). See also Temperature-viscosity Relations in the Ternary System CaO-Al_2O_3-SiO_2, U. S. Bur. Mines *Tech. Paper* 189 (1919).

[6] P. H. Royster, and T. L. Joseph: Pyrometry in Blast-furnace Work. *Trans.*, A. I. M. E. (1921) Pyrometry, 544.

[7] R. H. Sweetser: Barium Oxide in Blast-furnace Slag. *Iron Age* (1910) **85**, 259.

Other average operating information over a 17-day period follows:

Iron per day, tons	286.6
Coke per ton, lb	1888.0
Limestone per ton, lb	714.0
Yield, per cent	57.4
Silicon in pig iron, per cent	1.27
Sulfur in pig iron, per cent	0.023
Phosphorus in pig iron, per cent	0.088
Silica in slag, per cent	30.21
Alumina in slag, per cent	13.20

The BaO came from a nodulized "blue billy" containing 59.65 per cent. Fe and 3.15 per cent. BaO.

Hofman,[8] in discussing silicate slags, mentioned the powerful fluxing action of barium oxide in lowering the formation temperatures of silicates, but also stated that barium oxide did not increase the fluidity of the slag as the slags did not flow well. Detailed information on the temperature-viscosity relations of slags containing barium oxide is lacking. A comparison of reported melting points[9] of the alkaline earth oxides and of the metasilicates of barium and calcium follows:

	Melting Point, Deg. C.		Melting Point Deg. C.
BaO	1923	$BaSiO_3$	1465
SrO	2430	$CaSiO_3$	1540
CaO	2570		

These meager data on melting points of silicates are of little value without viscosity data which indicate the changes in the free-running characteristics of slags at various temperatures.

Experimental Procedure and Description of Apparatus

Because it was impossible to duplicate blast-furnace conditions in the laboratory the best method of obtaining comparative results appeared to be to determine the rate at which sulfur was absorbed by average blast-furnace slag and slags containing small quantities of BaO under a set of arbitrarily defined conditions, discussed later. Such a series of laboratory experiments should indicate the order of desulfurization by the various slags in the blast furnace.

It seemed desirable to determine the relative proportions of sulfur absorbed under comparable conditions of temperature and composition

[8] H. O. Hofman: Temperatures at Which Certain Ferrous and Calcic Silicates are Formed in Fusion, and the Effect upon These Temperatures of the Presence of Certain Metallic Oxides. *Trans.*, A. I. M. E. (1899) **29**, 705.

[9] H. O. Hofman: General Metallurgy, 463. 1913. McGraw-Hill Book Co., Inc.
E. E. Schumacher: Melting Points of Barium, Calcium, and Strontium Oxides: *Jnl.* Chem. Soc. (1926) **48**, No. 2, 396.

by the slag while in contact with a bath of molten metal, also when fine streams of metal were poured through a column of molten slag. Two types of experiments to make this comparison of method of contact between slag and metal are designated hereafter as the "bath" and "dropping" types. It was believed that a viscous slag would decrease the rate

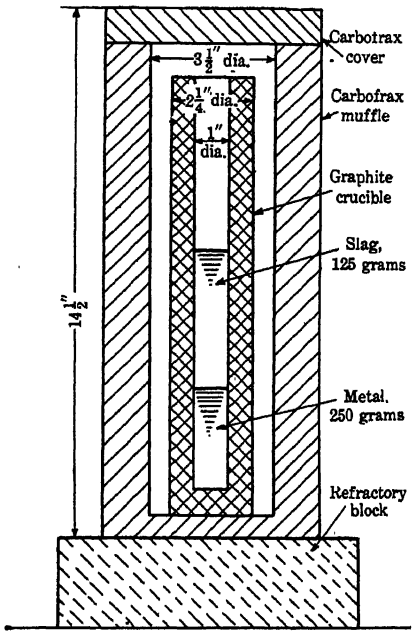


FIG. 1.—SET-UP FOR MAKING BATH-TYPE TESTS.

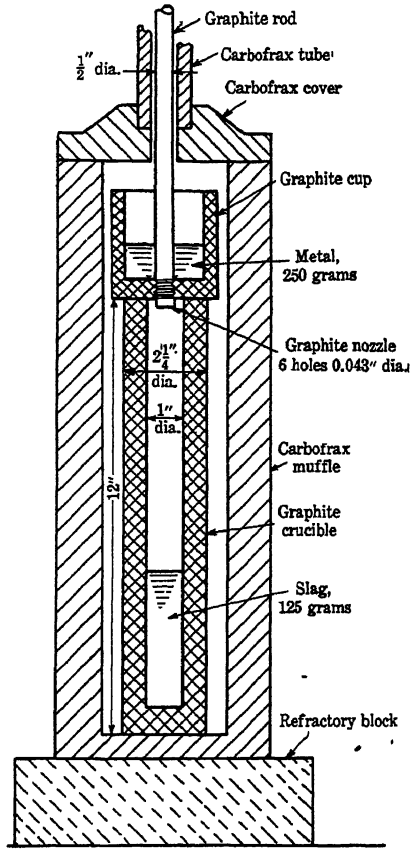


FIG. 2.—SET-UP FOR MAKING DROPPING TESTS.

at which sulfur was absorbed by the slag in the bath test, due to a slowing down of the rates of diffusion of the products of the reaction:

$$FeS + CaO + C \leftrightarrows CaS + CO + Fe.$$

On the other hand, it was thought that viscosity would aid sulfur elimination in the dropping test because a viscous slag would retard the rate of fall of the metal through the slag and increase the time of contact of slag and metal. Plans were made to study the effect of viscosity on sulfur elimination in the two types of experiments, but the investigation was abandoned before viscosity determinations were made.

The crucibles used were made of Acheson graphite, which seemed to be the only material that would withstand the action of the slag at the temperatures employed. Another advantage in using graphite was that it produced a reducing atmosphere in the crucible, making conditions in this respect similar to those in the hearth of a blast furnace. As an electric furnace was not available at the Experiment Station, it was necessary to build a high-temperature, oil-fired muffle furnace to prevent excessive oxidation of the graphite. The construction details and operation of this furnace were described in a previous report.[10] It was possible to maintain in this furnace constant temperatures within the range of

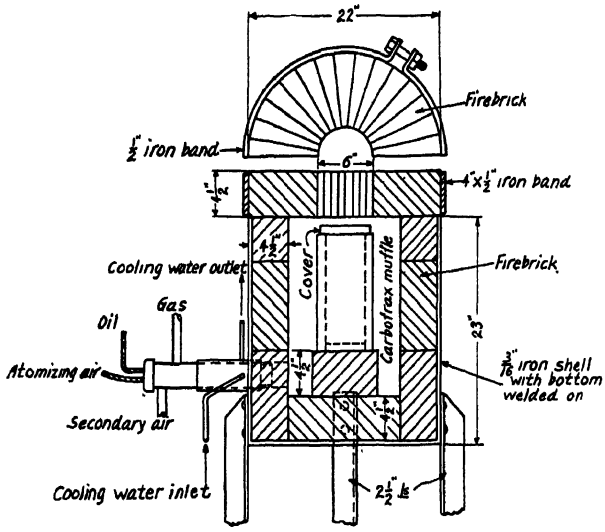


FIG. 3.—SECTION OF FURNACE.

1400° to 1650° C. Temperature measurements were made with an optical pyrometer which had been checked with a platinum, platinum-rhodium thermocouple at several temperatures between 1300° and 1450° C.

Bath-type Tests

Figs. 1 and 3 show the apparatus employed in making the bath tests. The graphite tube containing the charge of metal was first placed in the furnace and heated to the desired temperature, then the pulverized slag was poured on top of the molten metal and the test continued for the specified period. Then the crucible was removed and the contents poured into an iron mold.

[10] E. P. Barrett and C. E. Wood: A Muffle-type Pot Furnace. *Chem. & Met. Eng.* (1928) **35**, 179.

Dropping-type Tests

Figs. 2 and 3 show the apparatus for making the dropping tests. In this case the slag was placed in the crucible and the metal in the graphite cup fitted with the nozzle and plug. When the desired temperature was reached the graphite plug was unscrewed and the metal allowed to run out of the cup through the nozzle, which contained six holes each 0.043 in. dia. No attempt was made to determine the exact time required for the metal to run out of the cup, but to secure uniform conditions 5 min. was allowed in each case; this was always found to be sufficient. Then the crucible and cup were removed and the charge poured into an iron mold as in the bath-type tests.

Combination of Bath and Dropping Tests

A third test, a combination of the bath and dropping test, was also performed. In this the contiguous layers of slag and metal were held at constant temperature for the desired time after the metal had been dropped through the slag. Tables 1, 2 and 3 are logs indicating the further procedure in each type of test. In each case 250 g. metal and 125 g. slag were used.

TABLE 1.—*Log of Bath-type Test, No.* 30

Time	Temperature, Deg. C.	Remarks
9:00		Started furnace on gas.
10:50		Turned on oil and charged metal.
11:50	1525	
12:00	1490	Added slag.
12:10	1490	
12:20	1500	
12:30	1490	
12:40	1500	
12:50	1520	
1:00	1510	Poured charge.

TABLE 2.—*Log of Dropping-type Test, No.* 35

Time	Temperature, Deg. C.	Remarks
1:00		Turned on oil.
2:30		Put charge in furnace.
2:45	1304	
3:00	1504	
3:15	1482	
3:30	1490	
3:40	1511	Removed plug.
3:45		Poured charge.

TABLE 3.—*Log of Combination-type Test, No. 49*

Time	Temperature, Deg. C.	Remarks
11:45		Turned on oil.
12:45	1520	Put charge in furnace.
1:00	1450	
1:15	1490	
1:25	1500	
1:35	1510	
1:45	1520	Removed plug.
1:55		
2:05	1510	
2:15	1520	
2:25	1490	
2:35	1490	
2:45	1510	Poured charge. Slag brown and opaque; more viscous than test No. 48.

COMPOSITION OF SLAGS

In practice barium oxide could be used so as to change the percentages of all the slag constituents according to the amount of BaO used; CaO could be replaced by BaO, and SiO_2 could be replaced with BaO, provided low-silica iron ore was available. Tables 4 and 10 show the composition

TABLE 4.—*Composition of Slags Used in Dropping and Bath-type Tests.*

Slag No.	SiO_2, Per Cent.	FeO, Per Cent.	Al_2O_3 Per Cent.	CaO, Per Cent.	MgO, Per Cent.	BaO, Per Cent	S, Per Cent.	Molar Ratio,* Bases to Acids
4016	36.26	0.84	14.07	45.95	3.50	none	0.075	1.23
4016*A*†	35.44	0.82	13.70	44.85	3.42	2.32	0.075	1.25
4016*B*†	34.58	0.80	13.40	43.76	3.34	4.72	0.075	1.27
4083	36.77	1.05	12.44	45.26	4.08	none	0.157	1.25
4084‡	31.34	1.03	11.44	46.40	3.78	5.17	0.135	1.51
4085	35.34	1.33	12.43	34.80	3.47	12.73	0.089	1.12

* Iron content of slag is neglected since it is present largely as metallic iron.

† Slags 4016*A* and 4016*B* were prepared by adding BaO to slag 4016.

‡ Molar basicity was calculated as follows for slag 4084:

	Moles of Acids				Moles of Bases		
SiO_2	31.34 ÷ 60.3	= 0.520		CaO	46.4 ÷ 56.0	= 0.827	
Al_2O_3	11.44 ÷ 102.2	= 0.112		MgO	3.78 ÷ 40.3	= 0.094	
				BaO	5.17 ÷ 153.4	= 0.034	
Total		0.632		Total		0.955	

Ratio, bases to acids $= \frac{0.955}{0.632} = 1.51.$

of the slags used. Slags 4016 and 4083 are in the range of composition of normal blast-furnace slag and were used to indicate the desulfurization which could be accomplished with normal slags under the conditions of the experiments. The effect of adding small amounts of barium oxide to normal slag and of changing all constituents accordingly was studied by the use of slags 4016*A* and 4016*B*, made by adding sufficient quantities of barium hydrate to slag 4016 to introduce 2.32 and 4.72 per cent. of BaO, respectively. Replacement of about 5 per cent. SiO_2 by BaO with a corresponding increase in molar basicity was investigated by the use of slag 4084. This slag was similar to the one reported by Sweetser. If CaO is replaced by BaO, the molar basicity is decreased due to the higher molecular weight of the latter. In slag 4085 about 12 per cent. CaO was replaced by BaO. Table 10 shows the composition of a series of slags in which CaO was almost completely replaced by BaO in 10 steps. In order to eliminate the effect of changes in molar basicity the molar ratio of bases to acids was held about constant in this series of slags.

Composition of Metal

The metal used in the first 26 tests contained 0.121 per cent. sulfur. This concentration of sulfur was selected because samples taken by Kinney from the interior of a 300-ton furnace indicate this is the order of the concentration of sulfur in the metal reaching the combustion zone. Normal experimental errors in determining sulfur by the usual gravimetric method represented such a large percentage of the total sulfur involved that satisfactory sulfur balances, which act as a check upon the work, were impossible. Other experimental errors were also enlarged on account of the small quantity of sulfur involved. In tests 27 to 38, inclusive, a higher concentration of sulfur was used. This made it possible to obtain better sulfur balances in the bath-type tests, but in the dropping-type tests loss of sulfur took place as the metal was coming up to temperature previous to its release and passage through the slag layer (see Tables 6 and 8).

Discussion of Results

In the first series of tests 250 g. metal containing 0.121 per cent. sulfur was held in contact with 125 g. slag for periods of 30, 45 and 60 min. and at temperatures of 1400° and 1500° C. Most of the tests were made at 1500° C. Duplicate tests were made using slag of about normal composition and the same slag after the addition of sufficient barium hydrate to introduce 2.32 and 4.72 per cent. BaO respectively.

Table 5 shows the desulfurization obtained in the bath-type tests. Normal slag removed slightly more sulfur in 30 min. contact at 1400° C. than the slags containing BaO. At 1500° C. the slags containing BaO

TABLE 5.—*Desulfurization Obtained in Bath-type Tests*

Test No.	Slag No.*	Contact, Min.	Temperature, Deg. C.	BaO in Slag, Per Cent.	Sulfur in Metal before Test, Per Cent.	Sulfur in Metal after Test, Per Cent.	Sulfur Removed from Metal, Per Cent.
1	4016	30	1400	None	0.121	0.075	38.0
2	4016	30	1400	None	0.121	0.074	38.6
3	4016*A*	30	1400	2.32	0.121	0.078	35.5
4	4016*A*	30	1400	2.32	0.121	0.069	43.0
5	4016*B*	30	1400	4.72	0.121	0.079	34.7
6	4016*B*	30	1400	4.72	0.121	0.076	37.2
7	4016	30	1500	None	0.121	0.069	43.0
8	4016	30	1500	None	0.121	0.069	43.0
9	4016*A*	30	1500	2.32	0.121	0.063	47.9
10	4016*A*	30	1500	2.32	0.121	0.063	47.9
11	4016*B*	30	1500	4.72	0.121	0.047	61.2
12	4016*B*	30	1500	4.72	0.121	0.063	47.9
13	4016	45	1500	None	0.121	0.060	50.4
14	4016	45	1500	None	0.121	0.049	59 5
15	4016*A*	45	1500	2.32	0.121	0.051	57.8
16	4016*A*	45	1500	2.32	0.121	0.046	62.0
17	4016*B*	45	1500	4.72	0.121	0.026	78.5
18	4016*B*	45	1500	4.72	0.121	0.034	71.8
19	4016	60	1500	None	0.121	0.017	86.0
20	4016	60	1500	None	0.121	0.021	82.6
21	4016	60	1500	None	0.121	0.016	86.8
22	4016	60	1500	None	0.121	0.018	85.1
23	4016*A*	60	1500	2.32	0.121	0.027	77.7
24	4016*A*	60	1500	2.32	0.121	0.031	74.4
25	4016*B*	60	1500	4.72	0.121	0.029	76.0
26	4016*B*	60	1500	4.72	0.121	0.035	71.0
27	4083	60	1500	None	0.837	0.455	45.6
28	4083	60	1500	None	0.837	0.467	44.2
29	4084	60	1500	5.17	0.837	0.411	50.9
30	4084	60	1500	5.17	0.837	0.404	51.8
31	4085	60	1500	12.73	0.837	0.532	36.4
32	4085	60	1500	12.73	0.837	0.487	41.8

* See Table 4 for slag composition.

removed more sulfur during the 30 and 45-min. periods, but in the 60-min. period more complete desulfurization was obtained with normal slag. These results are shown graphically in Fig. 4. They indicate that the addition of quantities of barium hydrate necessary to introduce up to about 5 per cent. BaO with a corresponding dilution of other constituents does not markedly affect the desulfurizing action of the slag. The introduction of 4.72 per cent. BaO changed the molar basicity from 1.23 for the standard slag to 1.27 for slag 4016*B*. Viewing the results as a whole it seems likely that the addition of small percentages of BaO to slags of

normal composition increases the desulfurizing action of the slags slightly by reason of the small change in the molar basicity of the slag.

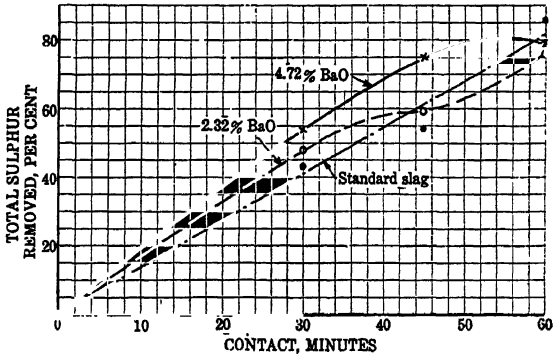


FIG. 4.—RELATION BETWEEN TIME OF CONTACT AND DESULFURIZATION.

Time of Contact between Slag and Metal

Tests 7 to 26, inclusive, made at 1500° C., show that time of contact has a pronounced effect upon the amount of sulfur removed from metal that is in contact with a quiescent layer of slag. Under the conditions of these experiments the sulfur removed varied almost directly with time

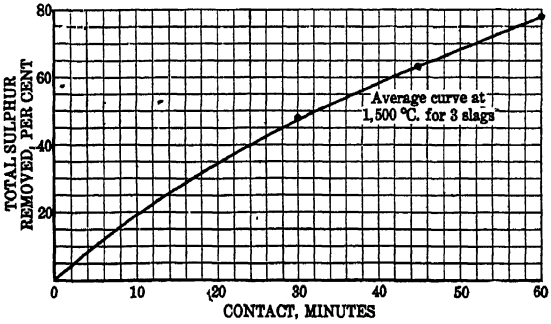


FIG. 5.—RELATION BETWEEN TIME OF CONTACT AND DESULFURIZATION.

over a 60-min. period. Fig. 5 shows that the average rate of transfer of sulfur from metal to normal slag and to slag containing 2.32 and 4.72 per cent. sulfur was somewhat more rapid over the first 30 min., but generally speaking the amount of sulfur eliminated varied directly with time of contact. Tests were not held long enough to reach equilibrium.

Replacement of Silica and Replacement of Lime with Barium Oxide

The addition of a few per cent. of BaO to blast-furnace slag changes the molar basicity to a limited extent. However, if silica is replaced by BaO as in slag 4084, a marked increase in molar basicity results. A sub-

TABLE 6.—*Sulfur Balance for Bath-type Tests*

Test No.	S in Charge,* G.	Sulfur in Metal after Test, Per Cent.	Sulfur in Metal after Test, G.	Sulfur in Slag after Test, Per Cent.	Sulfur in Slag after Test, G.	Sulfur in Slag and Metal, G.	Sulfur Unaccounted for, G.	Sulfur Unaccounted for, Per Cent.
1	0.396	0.075	0.188	0.137	0.171	0.359	−0.037	− 9.35
2	0.396	0.074	0.185	0.155	0.194	0.379	−0.017	− 4.28
3	0.396	0.078	0.195	0.147	0.182	0.375	−0.021	− 5.30
4	0.396	0.069	0.173	0.153	0.191	0.364	−0.032	− 8.07
5	0.396	0.079	0.198	0.169	0.211	0.409	+0.013	+ 3.28
6	0.396	0.076	0.190	0.143	0.179	0.369	−0.027	− 6.82
7	0.396	0.069	0.173	0.146	0.182	0.355	−0.041	−10.30
8	0.396	0.069	0.173	0.157	0.196	0.369	−0.027	− 6.82
9	0.396	0.063	0.158	0.171	0.214	0.372	−0.024	− 6.06
10	0.396	0.063	0.158	0.161	0.201	0.359	−0.037	− 9.35
11	0.396	0.047	0.118	0.196	0.314	0.314	−0.082	−20.70
12	0.396	0.063	0.158	0.169	0.211	0.369	−0.027	− 6.82
13	0.396	0.060	0.150	0.172	0.215	0.365	−0.031	− 7.40
14	0.396	0.049	0.123	0.224	0.280	0.403	+0.007	+ 1.77
15	0.396	0.051	0.125	0.213	0.266	0.391	−0.005	− 1.26
16	0.396	0.046	0.115	0.227	0.284	0.399	+0.003	+ 0.76
17	0.396	0.026	0.065	0.268	0.335	0.400	+0.004	+ 1.01
18	0.396	0.034	0.085	0.243	0.304	0.389	−0.007	− 1.77
19	0.396	0.017	0.042	0.233	0.291	0.333	−0.063	−15.9
20	0.396	0.021	0.052	0.237	0.296	0.348	−0.048	−12.1
21	0.396	0.016	0.040	0.248	0.310	0.350	−0.046	−11.6
22	0.396	0.018	0.045	0.237	0.296	0.341	−0.055	−12.5
23	0.396	0.027	0.067	0.254	0.318	0.385	−0.011	− 2.78
24	0.396	0.031	0.077	0.252	0.315	0.392	−0.004	− 1.01
25	0.396	0.029	0.072	0.249	0.311	0.383	−0.013	− 3.28
26	0.396	0.035	0.087	0.244	0.305	0.392	−0.004	− 1.01
27	2.288	0.455	1.140	0.868	1.085	2.225	−0.063	− 2.76
28	2.288	0.467	1.170	0.834	1.042	2.212	−0.076	− 3.32
29	2.261	0.411	1.030	0.968	1.210	2.240	−0.021	− 0.92
30	2.261	0.404	1.010	0.971	1.215	2.225	−0.036	− 1.57
31	2.203	0.532	1.332	0.702	0.871	2.210	+0.007	+ 0.31
32	2.203	0.487	1.222	0.782	0.978	2.200	−0.003	− 0.13

* Weight of sulfur in charges were obtained as follows:

		Grams
Tests 1 to 26, incl.:	Metal, 250 g. × 0.00121 =	0.3025
	Slag, 125 g. × 0.00075 =	0.0940
	Total sulfur in charge =	0.3965
Tests 27 and 28:	Metal, 250 g. × 0.00837 =	2.092
	Slag, 125 g. × 0.00157 =	0.196
	Total sulfur in charge =	2.288
Tests 29 and 30:	Metal, 250 g. × 0.00837 =	2.092
	Slag, 125 g. × 0.00135 =	0.169
	Total sulfur in charge =	2.261
Tests 30 and 31,	Metal, 250 g. × 0.00837 =	2.092
	Slag, 125 g. × 0.00089 =	0.111
	Total sulfur in charge =	2.203

stitution of about 5 per cent. BaO for SiO_2 changed the molar basicity from 1.25 for slag 4083 to 1.51 for slag 4084. When about 12 per cent. BaO was substituted for an equal percentage of CaO, the molar basicity decreased from 1.25 to 1.12, the decrease being due to the higher molecular weight of BaO.

Tests 27 to 38, inclusive, indicate that the desulfurizing action of slag under the condition of these tests varied almost directly with its molar ratio of bases to acids. Table 7 shows the observed values for percentage of sulfur and the calculated values based upon the variation in molar basicity from that of standard slag 4083.

From these laboratory tests one would expect the slag used in commercial practice by Sweetser to desulfurize more rapidly than normal slag. The molar ratio of bases to acids in Sweetser's slag was 1.54. This is slightly higher than the basicity of slag 4084, which gave comparatively rapid desulfurization. Desulfurizing action cannot be definitely related to any one slag constituent but is a function of the physical and chemical properties resulting from the combination of the principal slag constituents.

TABLE 7.—*Relation between Molar Basicity and Desulfurization*

Slag No.	Molar Ratio, Bases to Acids	Initial Sulfur in Metal, Per Cent.	Bath-type Tests, 60 Min.			Dropping-type Tests, 5 Min.		
			Sulfur in Metal after Test, Per Cent.	Initial Sulfur Eliminated Per Cent.	Calculated Sulfur Eliminated,* Per Cent.	Sulfur in Metal after Test, Per Cent.	Initial Sulfur Eliminated, Per Cent.	Calculated Sulfur Eliminated, Per Cent.
4085	1.12	0.837	0.510	39.1	40.25	0.633	24.4	24.3
4083	1.25	0.837	0.461	44.9	44.9	0.610	27.2	27.2
4084	1.51	0.837	0.407	51.4	54.2	0.490	41.5	32.9

* $\frac{\text{Molar ratio, bases to acids}}{\text{Molar ratio, bases to acids of standard slag}} \times$ observed percentage of sulfur eliminated by standard slag

Results on Dropping-type Tests

This type of test shows that surface contact between slag and metal has an important bearing on desulfurization. Table 8 shows the desulfurization obtained and Table 9 the sulfur balances. Duplicate tests did not agree as well as in the bath-type tests. This was probably due to variations in the flow of metal through the nozzles and the surface exposed during passage through the slag. An average of 27.2 per cent. of the sulfur in the metal was eliminated by slag of about normal composition in less than 5 min. by passing 250 g. metal at 1500° C. through a layer of slag about 4½ in. deep. The exact time required for the metal to pass through the slag was not determined, but it was less than

5 min. In 60 min. contact in the bath-type tests this same slag removed 44.9 per cent. of the initial sulfur in the metal. Slag 4084, in which silica was replaced with about 5 per cent. BaO, removed 41.5 per cent. of the total sulfur in less than 5 min. in the dropping tests as compared to 51.4 per cent. in 60 min. for the bath-type test. Slag 4085 removed 24.4 per cent. of the total sulfur in the dropping tests and 39.1 per cent. in the bath test.

TABLE 8.—*Desulfurization Obtained in Dropping-type Tests*

Test No.	Slag No.	Temperature, Deg. C.	BaO in Slag, Per Cent.	Sulfur in Metal before Test, Per Cent.	Sulfur in Metal after Test, Per Cent.	Total Sulfur Removed from Metal, Per Cent.
33	4083	1500	None	0.837	0.646	22.8
34	4083	1500	None	0.837	0.575	31.3
35	4084	1500	5.17	0.837	0.455	45.6
36	4084	1500	5.17	0.837	0.526	37.2
37	4085	1500	12.73	0.837	0.633	24.4
38	4085	1500	12.73	0.837	0.634	24.3

NOTE.—Tests were poured 5 min. after metal started dropping through the slag.

TABLE 9.—*Sulfur Balance for Dropping-type Tests.*

Test No.	Sulfur in Charge, G.	Sulfur in Metal after Test, Per Cent.	Sulfur in Metal after Test, G.	Sulfur in Slag after Test, Per Cent.	Sulfur in Slag after Test, G.	Sulfur in Slag and Metal, G.	Sulfur Unaccounted for, G.	Sulfur in Charge Unaccounted for Per Cent.
33	2.288	0.646	1.620	0.494	0.616	2.236	−0.052	− 2.27
34	2.288	0.575	1.440	0.486	0.607	2.047	−0.041	− 1.79
35	2.261	0.455	1.140	0.760	0.950	2.090	−0.171	− 7.55
36	2.261	0.526	1.319	0.641	0.801	2.120	−0.141	− 6.23
37	2.203	0.633	1.158	0.372	0.465	1.623	−0.580	−26.4
38	2.203	0.634	1.159	0.476	0.595	1.754	−0.449	−20.4

Although no viscosity measurements were made on the three slags, observations at the time they were poured after the tests indicated that slag 4085 was the most viscous. The removal of more sulfur by this slag than by slags 4083 and 4084 was probably due to its higher viscosity and somewhat greater density, as well as to its higher molar basicity. According to Stokes's law for falling bodies, which Feild and Royster[11] applied to the movement of globules of iron through a layer of slag, the velocity of the iron globules varies inversely with the first power of the slag viscosity and directly as the difference between the density of the

[11] A. L. Feild and P. H. Royster: Slag-viscosity Tables for Blast-furnace Work. U. S. Bur. Mines *Tech. Paper* 187 (1918) 16.

metal and slag. The work of these investigators on slag viscosity shows that viscosity changes of several hundred per cent. often accompanied a comparatively small change in the percentage of the various slag constituents. One would expect that a change in viscosity discernible by pouring tests would markedly affect the sulfur eliminated in the dropping-type tests.

Effect of Viscosity on Desulfurization in the Blast Furnace

The effect of slag viscosity on desulfurization in the blast furnace depends on the relative amount of sulfur removed as the metal globules fall through the slag and as the contiguous layers of slag and metal exist in the crucible. If, as advocated by Herty and Gaines,[12] the major portion of desulfurization takes place as the metal globules fall through the slag, then one would expect viscosity to increase desulfurization. The results of the dropping-type tests, although admittedly incomplete, show the effect of increasing the surface contact between slag and metal in speeding up desulfurization. Although the time of contact was short, the surface exposed was comparatively large. The conditions in the laboratory experiment only remotely approached those in the crucibles of blast furnaces; for example, the layer of slag was shorter and contained no coke to retard the descent of the iron globules.

McCaffery and Oesterle[13] have expressed the opinion that the time factor is of greatest consequence in desulfurization. A progressive increase in the sulfur content of samples from the first flush after cast, succeeding flushes, and the slag at cast were cited to show the importance of time of contact. The bath-type tests show the importance of time of contact, but the data do not show that the major part of the sulfur is removed as the layers of slag and metal come in contact in the crucible of a blast furnace. If such is the case, increased slag viscosity retards desulfurization due to slower rates of diffusion.

Slag of about normal composition removed 70.8 per cent. of the total sulfur when the effects of the passage of globules of iron through the slag and 60 min. contact as quiescent layers were combined (see test 39, Table 10). Similar slag removed 44.9 per cent. of the total sulfur in the bath-type test and 27.2 per cent. in the dropping-type test, the total of the separate effects being 72.1 per cent. (see Table 7). It appears that sufficient data are not available clearly to establish the relative amounts of sulfur eliminated as the globules of iron pass through the slag and as the two materials exist as layers.

---

[12] C. H. Herty, Jr. and J. M. Gaines, Jr.: Desulphurizing in the Blast Furnace. *Blast Furnace & Steel Plant* (1928) **16**, 233.

[13] R. S. McCaffery and J. E. Oesterle: Desulphurizing Power of Iron Blast-furnace Slags. *Trans.*, A. I. M. E. (1923) **69**, 631.

Substitution of BaO for CaO without Changing Molar Basicity

Tests 39 to 49, inclusive, were made on a slag of about normal composition, and on 10 others in which CaO was replaced by BaO, approximately mol for mol. The composition of the slags used, the initial sulfur in the metal, and the desulfurization obtained are given in Table 10. A procedure, combining the passage of the metal through the slag as globules and subsequently holding the layers of slag and metal for 60 min., was followed in these tests. In view of the large change in the percentage composition of the slags, the variation in the sulfur removed is surprisingly small, particularly for slags in tests 42 to 49. The last eight slags represent a change in SiO_2 from 30.34 to 20.54 per cent., a change in Al_2O_3 from 10.63 to 7.47 per cent., a change in CaO from

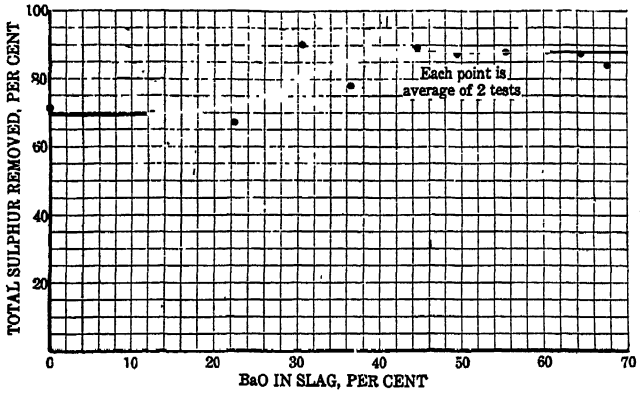


Fig. 6.—Effect of Replacing CaO with BaO on desulfurization.

23.66 to 1.12 per cent., a change in MgO from 4.05 to 2.45 per cent., and a change in BaO from 30.62 to 67.90 per cent. With the exception of test 43, the variation in total sulfur eliminated was only a few per cent. Fig. 6 shows graphically the variation in sulfur removed as the percentage of BaO in the slag changed. The introduction of BaO up to 22.3 per cent. produced little change in the amount of sulfur removed. As the BaO was increased from 22.3 to 30 per cent. the amount of sulfur eliminated increased. Beyond this point further substitution of BaO for CaO had little, if any, effect upon desulfurization.

This series of tests, in which a small variation in sulfur eliminated accompanied large changes in percentage composition when the molar basicity was held about constant, adds further support to the conclusion that the molar basicity is very closely related to desulfurization. The usual method in the industry is to figure slag basicity on the basis of the percentage of total bases and acids. Slag in test 48 contained 70 per cent. total bases and would therefore be considered a very basic slag. The molar basicity of this slag is the same as that of the normal slag

used in test 39 and which contained only 48.31 per cent. total bases. This comparison shows the importance of calculating basicity in terms of mols, particularly when dealing with a substance of such high molecular weight as barium oxide. It seems that any special merit that BaO may have over CaO as a desulfurizing agent would have been disclosed by these tests.

TABLE 10.—*Effect of Replacing CaO with BaO on Desulfurization**

Test No.	Composition of Slags, Per Cent.						Molar Ratio, Bases to Acids	Desulfurization Obtained			
	SiO_2	FeO	Al_2O_3	CaO	MgO	BaO		Initial Sulfur in Metal, Per Cent.	Sulfur after Test,† Per Cent.	Initial Sulfur Removed, Per Cent.	Average Temperature, Deg. C.
39	37.15	1.48	13.61	42.85	5.46	None	1.20	0.837	0.238	71.5	1500
40	35.15	1.38	12.14	34.45	4.96	12.60	1.17	0.837	0.251	70.1	1507
41	32.87	1.16	11.12	28.77	4.41	22.30	1.19	0.837	0.272	67.5	1497
42	30.34	1.05	10.63	23.66	4.05	30.62	1.19	0.837	0.082	90.2	1505
43	29.14	0.96	10.24	19.60	3.81	36.60	1.17	0.837	0.179	78.6	1495
44	27.00	0.87	9.74	14.97	3.34	44.50	1.18	0.837	0.086	89.8	1500
45	25.87	0.70	9.45	11.47	3.26	49.70	1.17	0.837	0.102	87.8	1492
46	24.11	0.67	8.74	8.41	2.98	55.35	1.20	0.837	0.100	88.2	1505
47	23.00	0.70	8.27	5.20	2.76	60.65	1.20	0.837	0.086	89.8	1500
48	22.19	0.44	7.98	2.90	2.60	64.50	1.20	0.837	0.107	87.2	1505
49	20.54	0.73	7.47	1.12	2.45	67.90	1.27	0.837	0.129	84.6	1505

* Combination of dropping and bath-type tests.
† Average for two tests.

SUMMARY

The experimental data obtained, although incomplete, indicate that:

1. The addition of sufficient quantities of barium hydrate to slag of normal composition to introduce up to 5 per cent. BaO into the slag does not markedly increase the desulfurizing action of the slag. Such an addition of BaO produces a small increase in the molar basicity of the slag and in its desulfurizing action.

2. The desulfurizing action of blast-furnace slag varies directly with its molar basicity. A replacement of SiO_2 by BaO increases the molar basicity of slag and therefore its desulfurizing action. A replacement of equal percentages of CaO by BaO decreases the molar basicity of the slag and its desulfurizing action. The industrial furnace slag referred to in the report had a slightly higher molar ratio of bases to acids than any of the slags used by the writers. Such slag would have more desulfurizing power than normal slag due primarily to its higher molar ratio and not to the BaO.

3. The desulfurizing action of a slag is more closely related to the molar ratio of bases to acids than to basicity based upon percentages of

bases and acids present, particularly when a substance of high molecular weight like BaO is involved.

4. Desulfurization of metal by contiguous layers of slag was almost directly proportional to time of contact over a period of 60 minutes.

5. Surface contact between slag and metal has an important bearing upon desulfurization, as shown by the amount of sulfur removed when globules of iron were passed through a layer of slag. Under similar conditions of temperature, quantities of metal and slag, and concentrations of sulfur, from 60 to 80 per cent. as much sulfur was removed in less than 5 min. when globules of iron were passed through a layer of slag as was removed during 60 min. contact between quiescent layers of slag and metal.

6. Barium oxide is about one-third as effective as an equal weight of CaO in removing sulfur and in fluxing SiO_2 and Al_2O_3. It was not determined whether the molar basicity of blast-furnace slag can be increased by the addition of BaO to such an extent as to have an appreciable effect upon the rate of desulfurization without producing a slag that is too viscous from other angles of practice.

Acknowledgments

The writers wish to acknowledge the assistance given by the Commercial Chemical Co. through S. A. Sanford, which made this investigation possible. Helpful advice and criticism were given by A. C. Fieldner, Chief Engineer of the Experiment Stations Division of the Bureau of Mines, and by C. H. Herty, Jr., Supervising Ferrous Metallurgist of the Bureau of Mines. At the Bureau's North Central Experiment Station much assistance in furnace operation and design was given by E. P. Barrett, metallurgist, and in temperature measurements by C. C. Furnas. W. F. Holbrook, chemist, assisted with the analyses.

DISCUSSION

C. S. Forkum, Donora, Pa. (written discussion).—The numerous tests made indicate to me that it is impossible in blast-furnace operations to make a barium oxide substitution in blast-furnace slags. This paper is interesting in that it seems to show that the desulfurizing action of blast-furnace slags is closely related to the molecular ratio of bases to acids. There are so many different slag combinations in blast-furnace operations that it seems to me impossible to designate one element as the principal desulfurizing element in blast-furnace slags.

In a blast-furnace slag of from 18 to 20 per cent. of alumina and magnesia contents of under 3 per cent., the alumina acts as a base and will control the sulfur content. The amount of manganese in blast-furnace slag has a very marked effect on the controlling of sulfur in the iron. From the use of open-hearth slag we obtain a manganese content in basic iron of about 1.75 per cent.; we produced last year, on our No. 2 furnace, 99.5 per cent. of the iron under 0.050 sulfur and 95 per cent. of the iron on the same furnace was under 0.040 sulfur. These results we obtained by proper distribution within the furnace, which permits the formation of the proper slag.

Having obtained these results over a year's run, it does not seem advisable to make any change in the composition of blast-furnace slag. There are a number of ways in which sulfur and iron unite, which have a marked bearing on whether the iron can be desulfurized. This has been proved in the open hearth. Iron of high sulfur content made from a cold or poorly working furnace can not be desulfurized in an open-hearth furnace, whereas good low-sulfur steel can be made from iron of a high sulfur content that is made on a good working furnace, where the sulfur content is due to water from a leaking tuyere. We have proved this a number of times.

Having obtained the results described, I do not see how it is possible to say that the substitution of one element for another will have the desired effect on the iron.

Metallic Electrodes for Cast-iron Arc Welding

By Shun-ichi Satoh,* Rigakushi, Tokyo, Japan

(New York Meeting, February, 1929)

The electric arc welding of cast iron has been studied by Braune, Lamberton, Schimpke, Kenyon, Gale Manufacturing Co., Wedemeyer, Candy, Neese, Miller, Carter, American Welding Society, Namack, Lebrun, Achenbach, Jansson, Kochendörffer and others.[1] The writer of this paper has been able to obtain a series of cast irons, from gray to white, without using cast-iron electrodes but by coating on wrought-iron bars mixtures of carborundum (SiC) and graphite (C). In this work, he found the curious phenomenon of barium carbonate.

---

* On research staff, Mitsubishi Research Laboratory.

[1] H. Braune: *Oest. Ztsch. f. Berg. u. Hüttenwesen*, **49**, 296. Quoted in *Jnl.* Iron and Steel Inst. (1901) **60**, 484.

D. E. Lamberton: Ueber das Schweissen des Gusseisens. *Stahl und Eisen* (1909) **29**, 2055.

P. Schimpke: Der heutige Standder neueren Schweissverfahren. *Stahl und Eisen* (1915) **35**, 385, 1274. Autogenes und elektrisches Schweissen von Gusseisen *Idem* (1926) **46**, 1141.

O. A. Kenyon: Welding Cast Iron with the Electric Arc. *Iron Age* (1920) **105**, 12.

Note on work of Gale Mfg. Co.: *Foundry* (1920) **48**, 383.

O. Wedemeyer: Schweissung von Gussstücken. *Stahl und Eisen* (1920) **40**, 1731.

A. M. Candy: Solving Arc Welding Problems. *Iron Tr. Rev.* (1921) **68**, 829.

H. Neese: Versuche über elektrische Lichtbogen-Schweissung von Flusseisen und Granguss. *Stahl und Eisen* (1922) **42**, 1192.

S. W. Miller: Fusion Welding. *Yearbook* Amer. Iron and Steel Inst. (1921) 287.

G. O. Carter: Dependability of Cast Iron Welding. *Iron Age* (1922) **109**, 928.

Problems in the Welding of Cast Iron. Amer. Weld. Soc. Meeting. *Iron Age* (1922) **110**, 929.

W. H. Namack: Electric Welding of Cast Iron. *Jnl.* Amer. Weld. Soc. (Nov., 1922) 7.

M. Lebrun: Note sur la soudure électrique de la fonte. *Rev. de Mét.* (1923) **20**, 248. Considérations théoriques sur la soudure électrique à l'arc. *Idem.* (1924) **21**, 484.

W. Achenbach: Lichtbogenschweissung von Gussstücken. *Giesserei Zeitung* (1924) **21**, 417.

A. H. Jansson: Welding Cast or Malleable Iron. *Iron Tr. Rev.* (1924) **74**, 1632.

H. Kochendörffer: *Stahl und Eisen* (1927) **47**, 703.

Preparation of Electrodes

Eleven wrought-iron bars 33 cm. long, 0.49 cm. dia. and 50 g. mean weight each were used as electrodes. The chemical analyses are given in Table 1.

Table 1.—*Analysis of Electrode*

	Per Cent.
Carbon	0.040
Silicon	0.054
Manganese	0.09
Phosphorus	Trace
Sulfur	0.02

Table 2.—*Coating Mixtures*

Number of Electrode	Graphite, Per Cent.	Carborundum, Per Cent.
0	100	0
1	90	10
2	80	20
3	70	30
4	60	40
5	50	50
6	40	60
7	30	70
8	20	80
9	10	90
10	0	100

Each of the bars, or electrodes, was wound with a twine of asbestos (1 mm. dia. weighing 0.5 g.) and then was coated with the mixtures listed in Table 2. The method used in coating was as follows: The mixtures were first reduced to paste by adding to them a solution of water glass (1:3), next they were put in a glass tube of 9 mm. inner diameter, with funnel-shaped mouth (shown in Fig. 1); then the bars were coated by passing them through the tube. The glass tube was used for the express purpose of making the diameters of all coated bars exactly 9 millimeters.

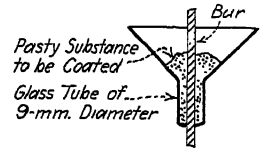


Fig. 1.—Tube with bar passing through coating mixture.

Electric Welding of Series Cast Iron

The cast iron was deposited on the steel plates by using the 11 kinds of electrodes mentioned. Each electrode was connected to the positive pole of the welding generator. In Fig. 2, which shows terminal voltage and current in this operation, the abscissa indicates the various

kinds of electrodes and the percentages of carbon and carborundum in the coating (the abscissas in Figs. 14 and 15 show the same), and the ordinate, voltage and ampere.

Figs. 3 to 13 show photomicrographs of deposit metals obtained from the 11 electrodes. The left-hand figures show the structures etched with 2 per cent. alcoholic nitric acid and those on the right show the unetched structures.

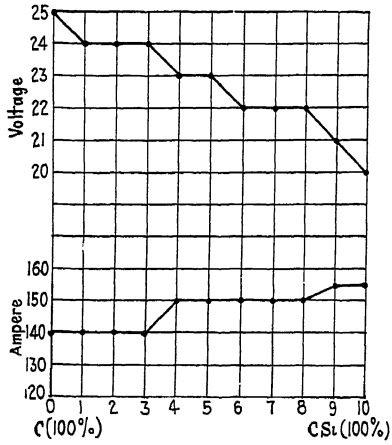


FIG. 2.—TERMINAL VOLTAGE AND CURRENT IN ELECTRIC WELDING OF SERIES CAST IRON.

Chemical analyses of all deposits obtained from 11 electrodes are shown in Table 3 and graphically in Fig. 14. The injurious effects of phosphorus and sulfur, which are usually found in ordinary cast iron, can not be found in the series cast iron obtained by the writer.

Brinell hardness numbers obtained as the result of the tests made under 3000-kg. load are shown graphically in Fig. 15.

PRACTICAL APPLICATION OF CAST-IRON WELDING

Deposits suitable for gray cast-iron welding were obtained by the use of electrodes 4, 5 and 6. The writer also made the following experiments.

Weight of Coating Required for an Electrode

With the object of knowing the necessary quantity of coating, the writer prepared: (1) an electrode (No. 6) by passing it through a glass tube of 9 mm. dia.; (2) another electrode (No. 6*a*) by passing it through a glass tube of 8 mm. dia. (this electrode was better than No. 6 electrode, since there was some superfluous coating on the latter); and (3) a third electrode (No. 6*b*) by passing it through a glass tube of 7 mm. dia. Welding with this last electrode, the writer obtained high-carbon steel

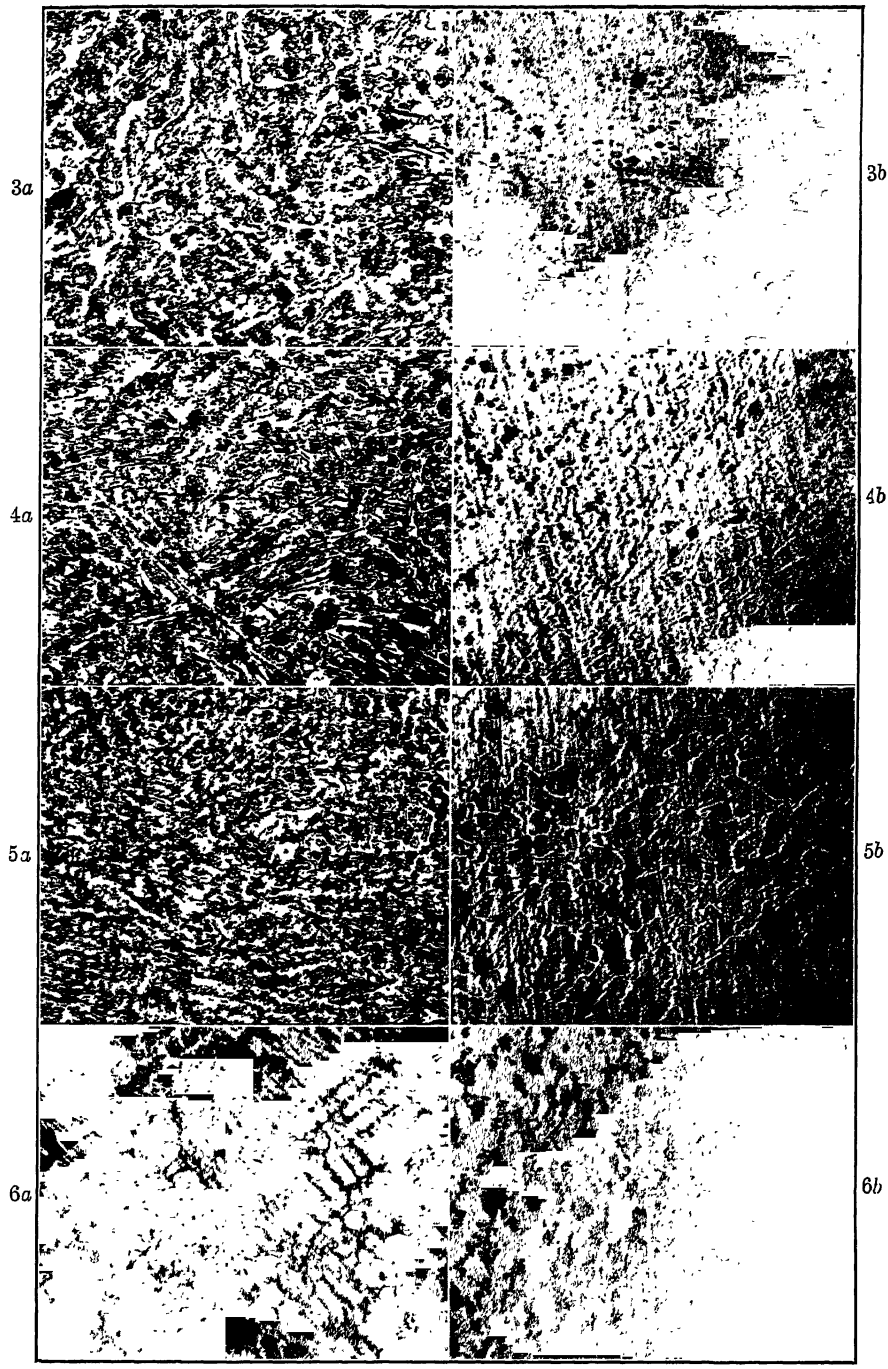


FIG. 3.—DEPOSIT METAL OBTAINED WITH NO. 0 ELECTRODE.
FIG. 4.—DEPOSIT METAL OBTAINED WITH NO. 1 ELECTRODE.
FIG. 5.—DEPOSIT METAL OBTAINED WITH NO. 2 ELECTRODE.
FIG. 6.—DEPOSIT METAL OBTAINED WITH NO. 3 ELECTRODE.

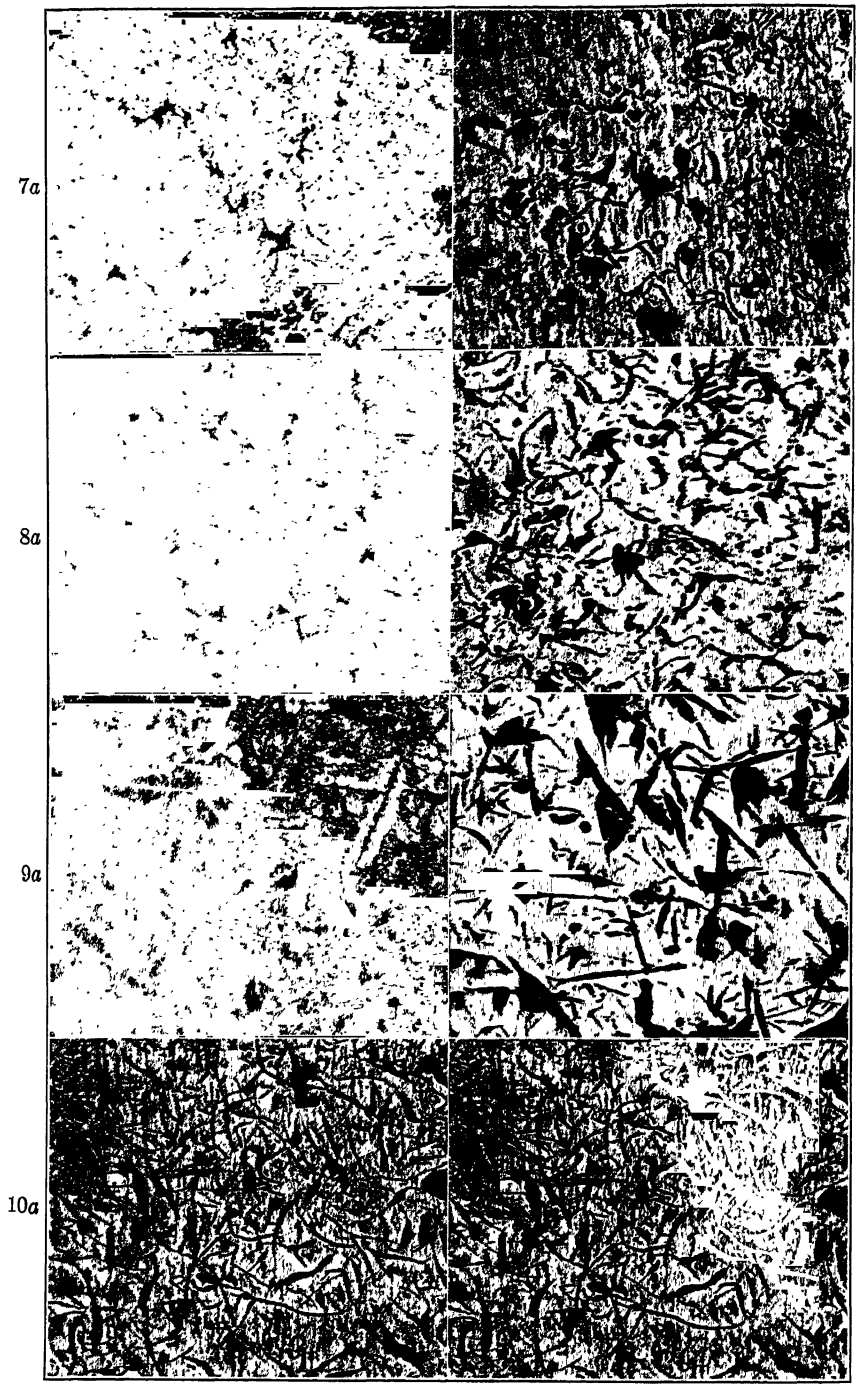


FIG. 7.—DEPOSIT METAL OBTAINED WITH NO. 4 ELECTRODE.
FIG. 8.—DEPOSIT METAL OBTAINED WITH NO. 5 ELECTRODE.
FIG. 9.—DEPOSIT METAL OBTAINED WITH NO. 6 ELECTRODE.

FIG. 11.—DEPOSIT METAL OBTAINED WITH NO. 8 ELECTRODE.
FIG. 12.—DEPOSIT METAL OBTAINED WITH NO. 9 ELECTRODE.
FIG. 13.—DEPOSIT METAL OBTAINED WITH NO. 10 ELECTRODE.

In each case, *a* was etched with 2 per cent. nitric acid; *b* was unetched. × 100.
All electrodes were connected to positive pole of welding generator.

deposit, which contains 1.31 per cent. total carbon, trace of graphite carbon and 1.68 per cent. silicon (see Fig. 16).

TABLE 3.—*Chemical Analyses of Deposits from the Coated Electrodes*

Number of Electrode	Total Carbon, Per Cent.	Graphite Carbon, Per Cent.	Combined Carbon, Per Cent.	Silicon, Per Cent.	Manganese, Per Cent.	Phosphorus, Per Cent.	Sulfur, Per Cent.
0	2.546	0.221	2.325	0.914	0.09	Trace	0.045
1	3.073	0.973	2.100	1.289	Trace	Trace	0.037
2	2.844	1.320	1.520	1.780	0.22	Trace	0.036
3	2.765	1.375	1.390	2.049	0.119	Trace	0.024
4	2.831	1.493	1.338	2.815	Trace	Trace	0.019
5	2.989	1.875	1.114	3.641	0.103	Trace	0.029
6	3.634	3.356	0.278	4.258	0.043	Trace	0.018
7	3.177	3.011	0.116	5.819	0.073	Trace	0.014
8	3.240	3.240	0	7.630		Trace	0.022
9	2.820	2.820	0	10.600		Trace	0.023
10	2.748	2.748	0	11.580		Trace	Trace

As may be seen, this No. 6*b* electrode does not answer the purpose as electrode for cast iron.

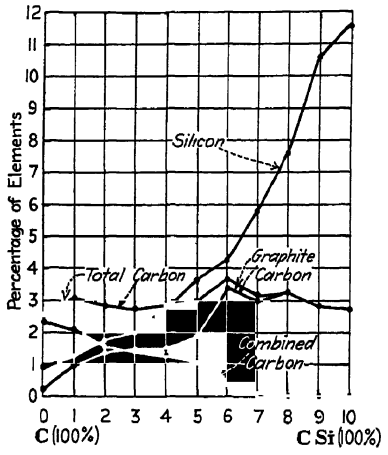


FIG. 14.—CHEMICAL ANALYSIS OF DEPOSITED CAST IRON.

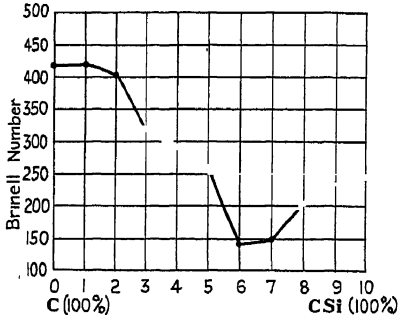


FIG. 15.—BRINELL NUMBERS OF DEPOSITED CAST IRON.

Influence of Calcined Borax, Calcium Carbonate and Barium Carbonate

In order to see what effect could be obtained by adding some substances to the coating of No. 6*a* electrode, the following test was made. The electrode was connected to the positive pole of the generator, and three coatings were used, containing respectively 3 per cent., 5 per cent. and 10 per cent. each of calcined borax, calcium carbonate and barium carbonate. No good results were obtained.

Influence of Preheating

The higher the preheating temperature, the easier becomes the operation.

TABLE 4.—*Time, Voltage and Amperes Required to Melt an Electrode*

Number of Electrode	Time, Minutes		Voltage		Ampere	
	(Electrode +)	(Electrode −)	(Electrode +)	(Electrode −)	(Electrode +)	(Electrode −)
6*a*	3½	2⅙	24	20	140	150
6*a* (3 per cent. borax)	3	2⅓	24	20	140	150
6*a* (3 per cent. $CaCO_3$)	3⅙	2½	24	22	140	145
6*a* (3 per cent. $BaCO_3$)	3	5½	24	22	140	130

Change of Polarity and Time Required to Melt an Electrode

In order to avoid preheating, if possible, the following experiments were made: The electrodes were connected to the negative pole of the generator, and cast iron was deposited with electrode 6*a* containing 3 per cent. calcined borax, another 6*a* electrode containing 3 per cent. calcium carbonate and a third 6*a* electrode containing 3 per cent. barium carbonate. Next, the electrodes were connected to the positive pole, and the same process of depositing was repeated, to see the difference of the voltage, amperes, and the time required to melt down one electrode. The figures representing the

FIG. 16.—DEPOSIT METAL OBTAINED WITH NO. 6*b* ELECTRODE CONNECTED TO POSITIVE POLE OF WELDING GENERATOR. ETCHED WITH 5 PER CENT. PICRIC ACID. × 100.

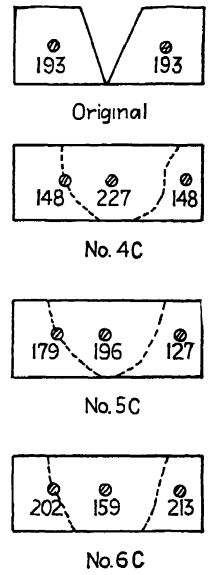


FIG. 17.—BRINELL NUMBERS AT WELDS.

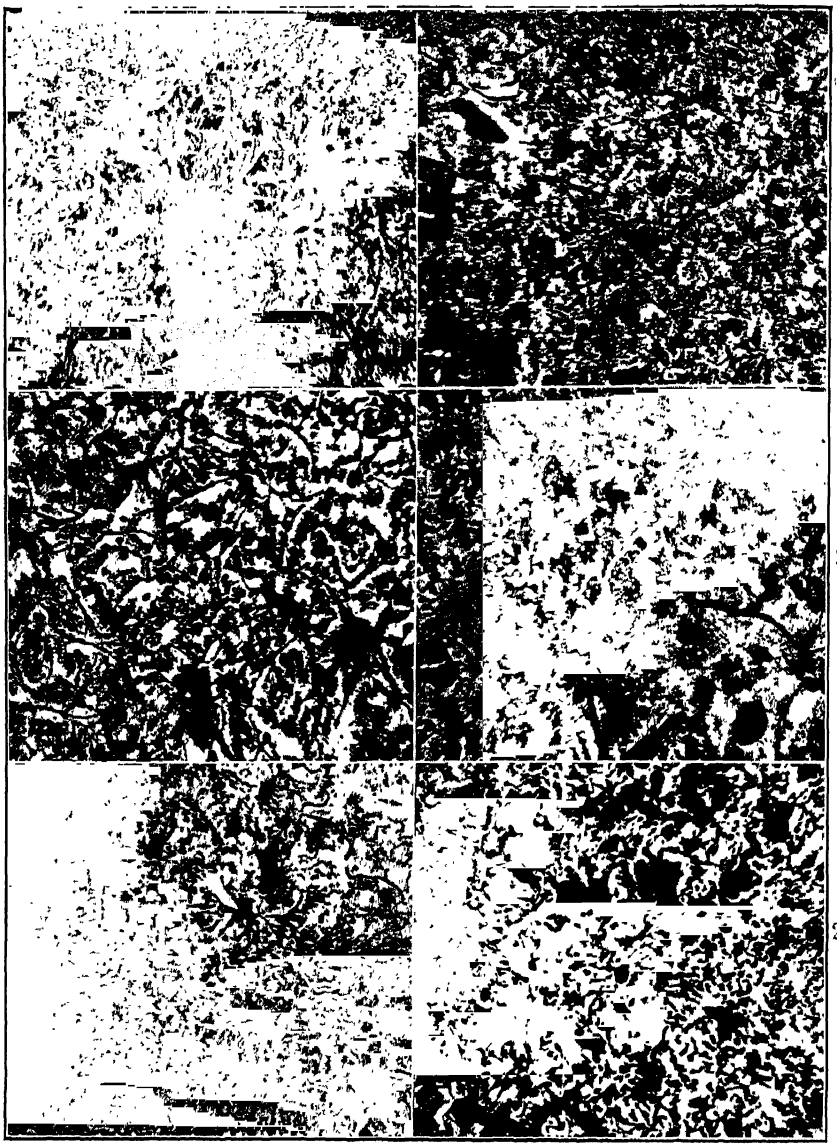


FIG. 18.—DEPOSIT METAL OBTAINED WITH NO. 4c ELECTRODE.
FIG. 19.—DEPOSIT METAL OBTAINED WITH NO. 5c ELECTRODE.
FIG. 20.—DEPOSIT METAL OBTAINED WITH NO. 6c ELECTRODE.
FIG. 21.—JUNCTION BETWEEN ORIGINAL CAST IRON AND DEPOSIT METAL OBTAINED WITH NO. 4c ELECTRODE.
FIG. 22.—JUNCTION BETWEEN ORIGINAL CAST IRON AND DEPOSIT METAL OBTAINED WITH NO. 5c ELECTRODE.
FIG. 23.—JUNCTION BETWEEN ORIGINAL CAST IRON AND DEPOSIT METAL OBTAINED WITH NO. 6c ELECTRODE.

All electrodes were connected to negative pole of welding generator.
All etched with 2 per cent. nitric acid. × 100.

voltage, amperes, and the time are given, in Table 4. Electrode 6*a* containing 3 per cent. barium carbonate alone, when connected to the negative pole, required an exceedingly long time for melting, or in other

FIG. 24.—ORIGINAL NONWELDED CAST IRON. ETCHED WITH 2 PER CENT. NITRIC ACID. × 100.

words, required greater electrical energy than for melting an electrode that does not contain barium carbonate; therefore it melted thoroughly. This requirement of long melting time will be quite analogous in result

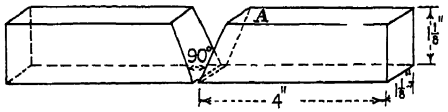


FIG. 25.—WELDED TEST PIECES FROM ELECTRODES 4, 5 AND 6.

with preheating, hence it was found that there is no need of preheating in this case. The writer thinks this fact very interesting. This phenomenon has occurred even with the admixture of 1 per cent. barium carbonate.

TABLE 5.—*Chemical Analyses of Welded Parts*

Number of Electrode	Total Carbon, Per Cent.	Graphite Carbon, Per Cent.	Combined Carbon, Per Cent.	Silicon, Per Cent.	Manganese, Per Cent.	Phosphorus, Per Cent.	Sulfur, Per Cent.
Original	3.413	2.689	0.724	1.905	0.286	0.251	0.04
4*c*	3.573	2.515	1.058	3.014	Trace	Trace	0.02
5*c*	3.906	3.402	0.504	4.317	Trace	Trace	0.02
6*c*	3.438	3.402	0.036	5.719	Trace	0.202	0.02

The writer has proved that the fusion of an electrode can be retarded by adding barium carbonate to the coating that covers the electrode. (It seems to him that no one before has noticed this phenomenon.)

It may not be rash to suppose that by choosing an appropriate coating, one can activate the fusion of an electrode—a fact that will be of great interest in the welding of steel. The writer has not succeeded in ascertaining the cause of this curious phenomenon. However, as it occurs when the electrode is set to the negative pole, it may be the one which the anion produces.

The Final Best Condition

Electrodes 4*a*, 5*a* and 6*a*, each containing 1 per cent. barium carbonate, are the best, and the writer now names these electrodes 4*c*, 5*c* and 6*c*. With electrodes 4*c*, 5*c* and 6*c* connected to the negative pole of the generator, cast-iron test pieces (original) were welded.

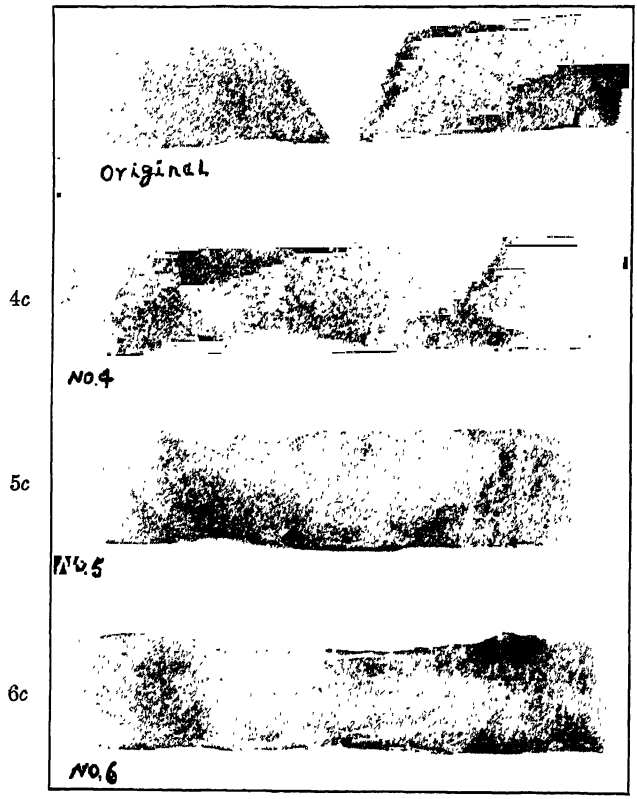


FIG. 26.—MACROSTRUCTURE OF ARC-FUSED METAL. UNETCHED. REDUCED APPROXIMATELY 15 PER CENT.

Chemical analyses of the welded parts and cast-iron test pieces are given in Table 5. Hardness tests are indicated in Fig. 17. There has never occurred, as shown here, any hard zone of cementite at the junction. Photomicrographs of the deposit metals obtained by the application of

electrodes 4*c*, 5*c* and 6*c* are shown respectively in Figs. 18, 19 and 20, and those of the junctions between the original cast iron and the deposits are shown respectively in Figs. 21, 22 and 23. Fig. 24 shows a photomicrograph of the original cast iron. In Fig. 26, the macrostructures of the cast iron, original and joints, are indicated.

Bending Tests of Final Best Cast Iron

Connecting electrodes 4*c*, 5*c* and 6*c* to the negative pole of the generator, cast-iron test pieces were welded (Fig. 25). From these welded bars, beams were cut, ¾ by ¾ by 8 in., and bending tests (span,

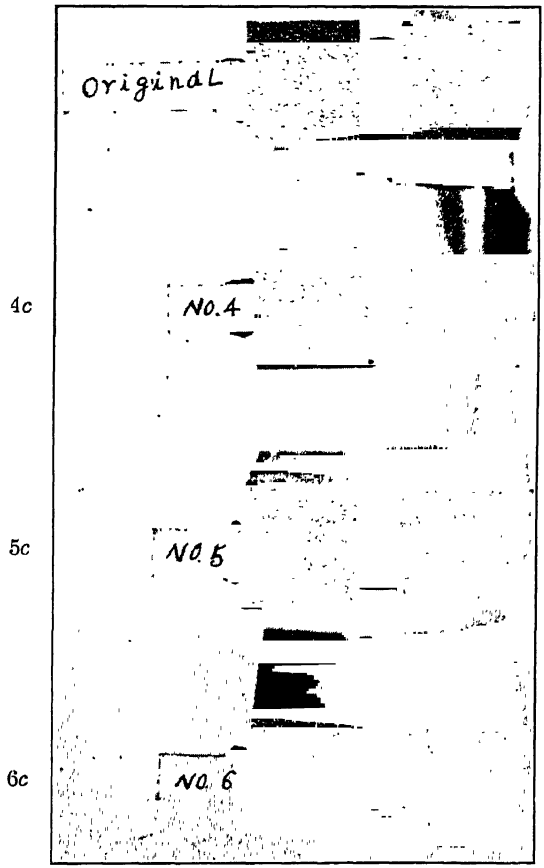


FIG. 27.—FRACTURES OF CAST-IRON BARS SUBJECTED TO BENDING TEST. ⅕ ORIGINAL SIZE.

6 in.) were conducted with the side *A* as tension side, using the optical mirror to indicate deflection. Modulus of elasticity and maximum stress calculated by these experiments are indicated in Table 6. The fractures of welded and nonwelded parts are shown in Fig. 27.

TABLE 6.—*Results of Bending Tests*

Number of Electrode	Modulus of Elasticity, Tons per Sq. In.	Maximum Stress, Tons per Sq. In.
Original	5310	22.4
4*c*	5330	26.2
5*c*	5320	24.3
6*c*	4990	19.1

Pressure Tests of Final Best Cast Iron

Hydraulic pressure tests were made by boring holes in the turbine casing, as shown in Fig. 28, and after they were welded as shown in Fig. 29, the result obtained was 230 lb. per square inch.[2]

SUMMARY

1. Various mixtures of graphite and carborundum were coated on wrought-iron bars and a series of cast iron, from gray to white, was deposited by using the coated bars as electrodes.

FIG. 28.—HOLES IN TURBINE CASING BORED BY HYDRAULIC PRESSURE TESTS.

2. Chemical analyses, hardness tests and microscopic examinations of the deposits were made and three kinds of electrodes were selected as suitable for gray cast-iron welding.

3. The optimum quantities of the coating towards the bars were determined and tests were made of the effect on welding of adding calcined borax, calcium carbonate and barium carbonate to the coating mixtures and also by changing the polarity. A curious phenomenon produced by barium carbonate was found; that is to say, it was found

[2] These tests were carried out by the help of Dr. Haramiishi.

that the fusion of the electrode can be retarded by adding barium carbonate to the coating that covers the electrode and by connecting this electrode to the negative pole of the generator.

4. As the best condition, the following results were obtained: Each of the three kinds of mixtures of 6:4, 5:5, 4:6 of graphite and carborundum and of 1 per cent. barium carbonate, was reduced to paste by the solution of water glass (1:3) and coated, through a glass tube of 8 mm. inner diameter, on electrodes 33 cm. long, 0.49 cm. dia, and 50 g. mean weight

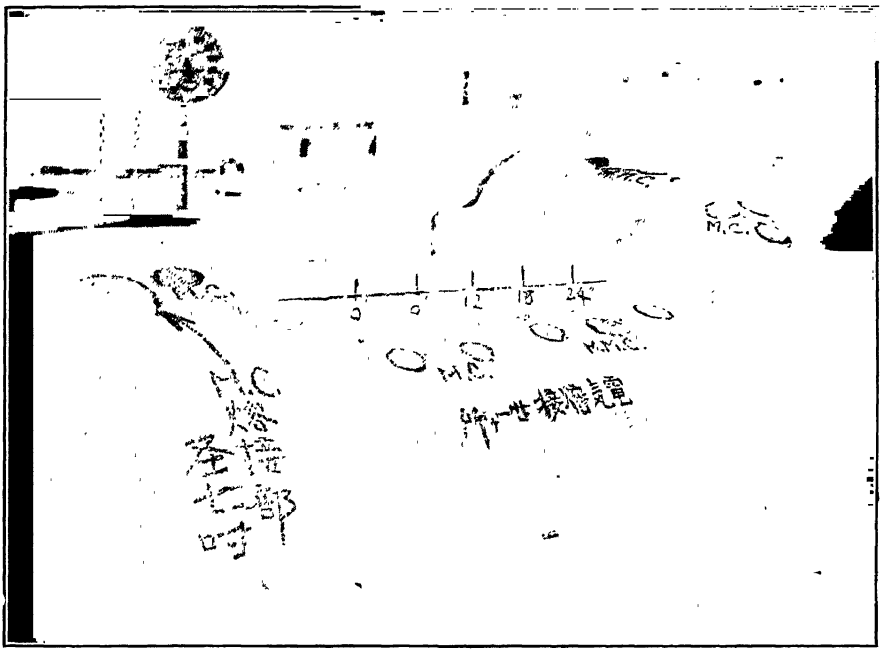


FIG. 29.—HOLES IN TURBINE CASING WELDED FOR PRESSURE TESTS.

each, wound with a twine of asbestos (1 mm. dia. weighing 0.5 g.). The electrode thus obtained is to be used, connected to the negative pole of the generator.

5. Chemical analyses, microscopic examinations, hardness tests, bending tests and pressure tests were conducted on the deposits of the best condition. The merit of the electrodes prepared by the writer is that deposits of cast iron of various composition, with low sulfur, low phosphorus and no hard zone can be obtained without preheating.

ACKNOWLEDGMENT

The writer wishes to thank Dr. K. Tawara, of Tokyo for his kind suggestion. He would also like to thank M. Lebrun, of Paris, for his warm interest in this paper.

DISCUSSION

M. LeBrun, Paris, France (written discussion*).—A noteworthy scientific method was used in the work done by Mr. Satoh. I have verified the results described, by making electrodes in accord with the author's specifications, and obtained gray cast iron that was perfectly machinable.

It should be mentioned that gray cast iron has already been obtained with the electric arc, either by using a cast-iron electrode covered by a coating high in carbon, as I described in a paper published several years ago in *Revue de Métallurgie*,[3] or by employing a regular coating high in carbon around a core of steel. This procedure was followed by Mr. Jones, director of the Society of Alloy Welding Processes. Like Mr. Satoh, Mr. Jones used an asbestos twine.

The value of Mr. Satoh's work, is that he has showed that by adding certain materials to the coating, such as barium carbonate, it is possible to retard considerably the duration of fusion of the electrode, by connecting it to the negative pole of the welding machine.

Mr. Satoh has introduced a new idea into the domain of electric welding. It is difficult, at present, to foresee all the consequences, but one may suppose that by broadening the application of this method, it may be possible to do successfully, with steel electrodes, work in which the difficulties of expansion and shrinkage have been insurmountable. Moreover, work along those lines will tend to accelerate the time of fusion of electrodes for other applications.

I hope that Mr. Satoh will persevere in his research. He will thus render great service to all methods of using electric arc welding.

The only criticism I would make of Mr. Satoh's paper is in regard to the omission of preheating for cast-iron welds. No matter what method is employed, preheating is always necessary, if the welds are to be sound and strong. Suppose that the piece to be welded is of small dimensions. The chamfer necessary to make a strong weld will always have a certain width. A shrinkage will result, which, if it is not compensated by preheating, during cooling will cause a fracture or will leave the piece under permanent strain.

Occasionally, with special conditions, successful welds have been made with cast iron without preheating, but this success has often been more apparent than real. The piece may have been satisfactory for the work demanded of it, but examination under the microscope would certainly have disclosed important defects.

The principal difficulty concerning electric welding of cast iron arises from the fact that this metal is not always the same. There is not, strictly speaking, cast iron; there are cast irons, of which the carbon content varies from 2 to 5 per cent.

P. A. E. Armstrong, New York, N. Y. (written discussion).—I do not think the action attributed to barium carbonate can be called a phenomenon. The solution of this apparent peculiarity is very simple. In Patent 1241899, filed by me in this country in March, 1915, and issued to me in 1917, I disclose electrodes for welding which are practically the same as those prepared by the author of this paper. I deposited by this method not only high-carbon irons of cast iron analysis, but various high-alloy steels including the present-day stainless steel; also various high-alloy irons and some nonferrous alloy metals.

The author's electrode is really a parallel circuit. The current flows through the iron core and also through the slag or coating at the molten end of the electrode. The conductivity of molten mixed silica and silicon carbide, iron carbide and carbon is

---

* Translated from the French.

[3] M. LeBrun: Considerations théoriques sur la soudure électrique á l'arc. *Rev. de Mét. Mem.* (1924) **21**, 484.

near to that of molten iron. The molten end of the electrode is in physical or electrical contact with the work, therefore the current has two paths to flow over: (1) the iron electrode; (2) from the iron electrode through the molten slag to the work. Each path carries a considerable amount of current.

More heat apparently is produced at the positive side of the arc; therefore it is an accepted fact that with bare wire or a very light slag-covered electrode, the work is the positive side but when the electrode is covered with a large amount of slag, such as layers of asbestos twine, etc., the electrode should be the positive side.

A slag-covered electrode will consume more energy per pound of metal melted than a bare electrode, because the slag has to be melted. This defect is compensated for by the more local character of the heat and the fact that the metal is not so readily wasted as vapor. This can be seen roughly by comparing the large amount of iron oxide deposited around the work, in the case of the bare iron electrode, against the very little, or even absence of iron oxide, in the case of the heavily slag-covered electrode.

The slag should be readily fusible, otherwise the iron electrode will burn up inside the solid slag coating. Further, the slag should be viscous from the solid part to the highly heated and very fluid slag deposit, which cannot be accomplished well without suitable flux.

The author's electrodes of SiC plus C addition are not as good conductors at the molten end as the SiC plus C suitably fluxed.

Calcium carbonate has a low melting point. In the presence of the heat of the arc it is fused with the silica and has a high melting point, therefore a small portion of the slag is fluid and carries current fairly well. Borax is a good solvent of oxide and does not make a good flux at high temperatures; although as a flux, as the author used it, it would not prevent energy flow through the molten slag.

Barium carbonate, although of a high melting point, will form in the presence of the arc and the silicon a silicate of comparatively low melting point and of good electrical conductivity when molten. When the barium carbonate SiC plus C electrode is the positive pole, the intense heat fuses the slag and melts the iron electrode. The melting end of the iron electrode is close to the work, the current flows down the iron electrode and part goes over the arc and part through the conductive slag coating at the fusing end. All the other slag electrodes work in approximately the same way.

If the electrode is negative, the iron core of the electrode melts up inside the slag coating and lengthens the arc, raising the voltage and lowering the amperage. The slag coating, because of the lower heat at the negative pole, is solid on the outside and does not carry current well; but it is molten or fusing on the inside and carries current very well. When the circuit is closed in this parallel circuit the current flows through the molten inside slag, uses up amperes and does not fuse the iron electrode quickly, because that is not where the current is being employed to an adequate extent.

Therefore in this instance, if a careful check is made of the total current flow, more energy is used when the negative is the electrode than when the positive is the electrode.

As will be seen in Table 4, the barium carbonate flux electrode as the negative pole used 15,730 watt-min., whereas a similar electrode as the positive pole used only 10,080 watt-min. The 50 per cent. greater power consumption did not flow over the metallic arc but through the slag; it heated up the work, hence preheating could be dispensed with. The difference is therefore due to the mechanical and electrical relationship of the electrode to the work and electrical conductivity of the slag and does not have anything to do with phenomena.

Many slags give similar results and the art of making heavy slag-covered electrodes is much concerned with the melting point and current-carrying capacities of the molten slag end.

I believe the action of the barium carbonate flux electrode can be thoroughly appreciated if the results obtained from an electrode of similar type is considered; for instance, if an iron electrode were fitted into a tube of carbon and the metal core connected to the negative side of the power and an arc struck between the end of this electrode and the work, the power would flow over the metallic core and through the carbon sleeve so that the arc would really be between the work and the two current paths of the electrode, one, of course, being the metal core and the other the carbon sleeve. Obviously the arc would melt the iron core a short distance up the carbon sleeve and then the arc would be maintained between the carbon sleeve and the work. Little or no power or arc would be between the metal core and the work. Under these circumstances a large amount of energy would be consumed in slowly melting the iron core which would not advance much more quickly than the rate at which the carbon sleeve was consumed or burned away. Of course, the instance I have given is an exaggeration, but it explains the action of the author's electrode in a practical manner.

I would suggest that the author use 30 to 50 volts across the arc, which with his heavy slag will give him a much better controlled electrode and a superior deposit, particularly when the work is of sizable mass and not a quickly heated small test piece.

*

Supplementary Notes on Metallic Electrodes for Cast-iron Arc Welding*

By Shun-ichi Satoh,† Tokyo, Japan

In the previous paper, the writer indicated that the arc welding of cast iron is practicable only when barium carbonate is used to retard the fusion of electrodes. Later, he tested the effects of 48 other elements, to discover the cause of their retarding action. Wrought-iron bars 33 cm. long and 0.53 cm. dia. were used as electrodes. The chemical analysis of the original electrode is given in Table 1.

Table 1.—*Analysis of Electrode*

	Per Cent.
Carbon	0.045
Silicon	0.028
Manganese	Trace
Phosphorus	0.047
Sulfur	0.008

Each of the bars was wound with a twine of asbestos (1 mm. dia., weighing 0.5 g.) and then was coated with a mixture of equal quantities of graphite and carborundum and one of the compounds listed in the second column of Table 2. The method used in coating was as follows: The mixtures were reduced to paste by adding to them a solution of water glass (1:3); they were next put in a glass tube of 8 mm. inner diameter, with funnel-shaped mouth (the same tube shown in the previous paper); then the bars were passed through the tube so that the mixtures were coated on them. The glass tube was used only as a means of making the diameters of all coated bars exactly 8 millimeters.

The cast iron was deposited on the steel plates by connecting the electrodes first to the positive and then to the negative pole of the generator. The figures representing the time, voltage, amperes and energy required to melt each electrode are given in Table 2. They are arranged in the order of the atomic weights of the elements contained in the coatings.

In Figs. 1 to 4, which show respectively the time, current, voltage and energy required in this operation, the abscissas indicate the atomic weights of the elements contained in the coatings, and the ordinates

* This paper is a supplement to the preceding one and is by the same author; see p. 144.

† On research staff, Mitsubishi Research Laboratory.

TABLE 2.—*Time, Voltage, Current and Energy Required to Melt an Electrode*

Test No.	Addition to Electrode		Time, Minutes		Voltage		Amperes		Wat
	Compound of Element	Per Cent.	Electrode +	Electrode −	Electrode +	Electrode −	Electrode +	Electrode −	Elec trod +
2	Li_2CO_3	2	2.63	2.29	24	26	146	133	153.
17[a]	$BeCl_2$	2	2.58	2.33	27	29	133	125	154.
46	$BeCO_3$	2	2.83	2.23	27	28	128	128	163.
40	B	2	2.50	2.13	24	28	145	120	145.
45	$Na_2B_4O_7$	2	2.73	2.33	23	27	143	128	149.
28	KF	2	2.64	2.66	22	27	150	130	145.
7	$Na_2CO_3.10H_2O$	2	2.69	2.18	23	28	145	128	149.
1[a]	$MgCO_3$	2	2.48	2.30	25	28	151	133	156.
23	Al_2O_3	2	2.84	2.39	24	26	138	130	156.
34[a]	P_2O_5	2	2.90	2.35	28	28	130	128	175.
39[a]	S	2	2.61	2.29	23	26	150	130	150.
43	KCl	2	2.58	2.24	22	27	153	130	144.
6	K_2CO_3	2	2.51	2.29	21	25	153	140	134.
47	$CaCO_3$	2	2.76	2.73	24	24	145	143	160.
14	TiO_2	2	2.50	2.35	23	24	146	135	139.
26	NH_4VO_3	2	2.59	2.26	21	27	151	123	136.
5	$CrCO_3$	2	2.56	2.13	22	27	151	135	141.
35	MnO_2	2	2.60	2.54	22	26	148	133	141.
36	Co_3O_4	2	2.59	2.10	23	28	148	123	146.
29[a]	$NiCl_2.6H_2O$	2	2.51	1.96	24	30	152	113	152.
21	CuO	2	2.57	2.19	23	29	143	120	140.
10	ZnO	2	2.79	2.40	26	28	136	127	164.
25	As_2O_3	2	2.72	2.41	23	27	138	123	143.
41	Se	2	2.18	2.00	23	30	150	110	125.
32	KBr	2	2.73	2.24	23	27	150	128	157.
50[a]	RbCl	2	2.75	2.51	25	27	143	128	163.
3	$SrCO_3$	2	2.54	3.17	22	22	153	142	142.
15	ZrO_2	2	2.49	2.20	22	29	154	123	140.
18	H_2MoO_4	2	2.73	2.10	22	30	149	113	149.
37	$PdCl_4$	2	2.55	2.14	21	28	150	120	133.
22	$AgNO_3$	2	2.60	2.18	23	28	145	123	144.
11	$Cd(C_2H_3O_2)_2.3H_2O$	2	2.59	2.39	24	28	135	130	139.
24	$SnCl_2.H_2O$	2	2.70	2.29	22	27	145	128	143.
27	Sb_2O_3	2	2.65	2.29	26	27	135	135	155.
42[a]	Te	2	1.97	1.85	22	30	150	110	108.
33	KI	2	2.71	2.34	25	28	142	125	160.
63	CsCl	2	2.86	3.25	20	22	155	145	147.
44	$BaCO_3$	2	2.81	4.63	22	22	148	150	152.
66[a]	$BaCO_3$	8	2.65	3.44	21	23	148	140	137.
67[a]	$BaCO_3$	32	2.38	3.38	20	20	155	150	123.
52	$Ba(C_2H_3O_2)_2.2H_2O$	2	2.61	2.88	22	25	145	135	138.
55	$BaCl_2.2H_2O$	2	2.57	4.44	22	22	150	140	141.
53	BaS	2	2.83	5.32	22	20	150	148	155.
57	$BaI_2.2H_2O$	2	2.50	4.49	22	21	155	155	142.
58	$BaBr_2.2H_2O$	2	2.65	4.55	20	21	160	153	141.
59	BaF_2	2	2.51	3.79	22	21	153	150	140.
54	BaO	2	2.69	4.71	22	22	150	143	147.
61[a]	BaO	8	2.79	3.99	21	20	150	145	146.
68	$BaSO_4$	0.4	2.36	4.44	19	21	170	158	127.
56	$BaSO_4$	2	2.86	5.45	20	22	153	141	145.
64	$BaSO_4$	8	2.64	5.08	20	22	153	145	134.
65[a]	$BaSO_4$	32	2.57	3.75	19	21	160	150	130.
48	$La(NO_3)_3.6H_2O$	2	2.40	2.41	23	25	150	133	138.
60	Ce_2O_3	2	2.81	2.28	21	24	150	130	147.
51[a]	$HTaO_3$	2	2.71	2.23	28	28	128	123	161.
20	WO_3	2	2.55	2.19	22	30	148	118	138.
30	OsO_4	2	2.52	2.00	21	29	155	120	136.
31	$PrCl_4.5H_2O$	2	2.53	2.15	22	30	153	113	141.
38	$AuCl_3.2H_2O$	2	2.61	2.09	23	28	150	125	150.
12	Hg_2Cl_2	2	2.63	2.13	22	29	147	118	141.
49	Tl_2SO_4	2	2.65	2.25	23	28	150	123	152.
19	$PbCO_3$	2	2.58	2.20	22	28	143	128	135.
4	$(BiO)_2CO_3$	2	2.28	1.92	23	30	148	120	129.
13	ThO_2	2	2.43	2.20	22	29	148	120	131.
16	$UO_2(NO_3)_2.6H_2O$	2	2.54	2.19	24	27	145	127	147.
9			2.54	2.25	24	27	137	130	139.

[a] Deposit metals obtained by connecting this electrode to the positive terminal resembl as fluidity in the liquid state is concerned, those obtained by connecting the electrode to the pole of the generator. .

indicate the time, amperes, voltage and energy; the points obtained by connecting the electrodes to the positive or negative pole of the generator

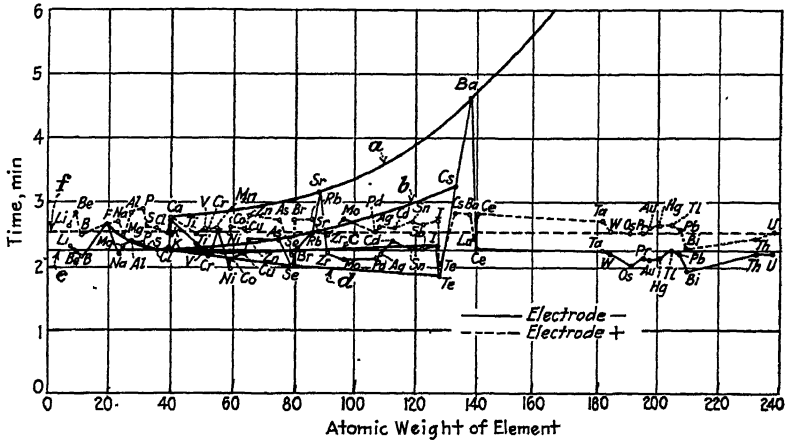


FIG. 1.—TIME REQUIRED TO MELT ELECTRODE CONTAINING SPECIAL ELEMENT.

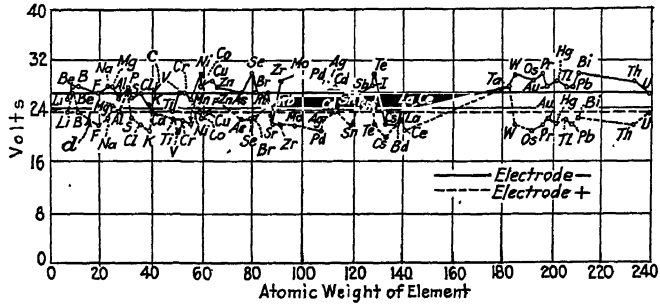


FIG. 2.—CURRENT IN ELECTRIC WELDING OF ELECTRODE CONTAINING SPECIAL ELEMENT.

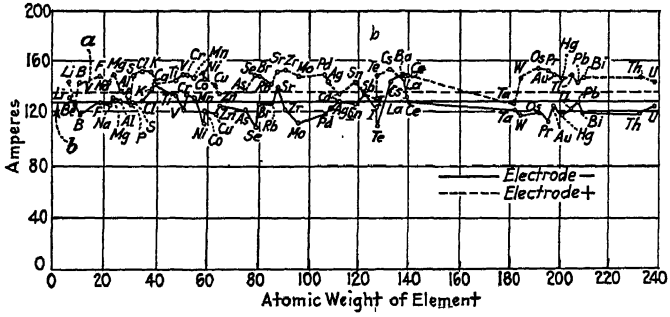


FIG. 3.—TERMINAL VOLTAGE IN ELECTRIC WELDING OF ELECTRODE CONTAINING SPECIAL ELEMENT.

are connected by the dotted or full lines; and the horizontal lines *f*, *a*, *d* (positive) and *e*, *b*, *c* (negative) are drawn through the points obtained

by using the electrodes that contained no special elements, in order to compare the specific effects of the elements.

When the coated electrodes containing alkali metals (*b* in Figs. 1 and 4) or alkaline earth metals (*a* in Figs. 1 and 4) were connected to the negative pole of the generator, the fusion of the electrodes was

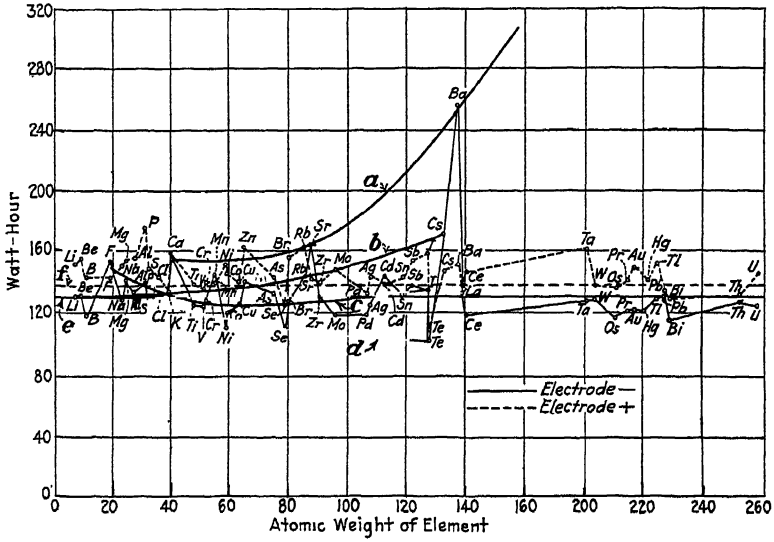


FIG. 4.—ENERGY REQUIRED TO MELT AN ELECTRODE CONTAINING A SPECIAL ELEMENT.

regularly retarded (*i. e.*, greater energy was required) in a successively increasing manner, as the atomic weight of either group increased. This action was especially marked with barium. The oxygen group (*d* in Figs. 1 and 4) produced an opposite effect on the fusion, that is, acceler-

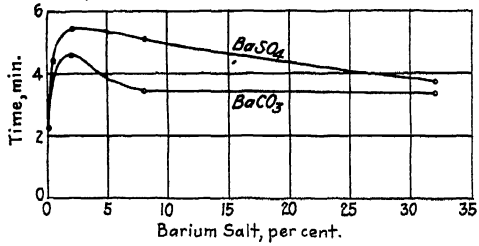


FIG. 5.—TIME REQUIRED TO MELT ELECTRODE CONTAINING BARIUM COMPOUNDS.

ated the fusion; halogen (*c* in Figs. 1 and 4) produced both effects; the other elements had no noticeable effect. A cursory glance at Figs. 1 and 4 will recall not only the relationships between the atomic weights and the atomic volumes, heats of formation of oxides and other various properties of elements,[1] but also will lead one to believe that if a radium

[1] J. A. N. Friend: Text Book of Inorganic Chemistry, 1, 273, London, 1919. Griffiin & Co., Ltd.

compound were added to the coating the fusion of the electrode would be more greatly retarded.

Tests of the relationship between the quantities of barium compounds and their respective retarding effect showed (Fig. 5) that 1 per cent. barium compound was sufficient to retard fusion of the electrode.

Finally, it was shown that the deposit metals obtained by connecting the electrodes (no matter whether special compounds were present or

(Positive electrode.) (Negative electrode.)

FIG. 6.—DEPOSIT METALS OBTAINED WITH ELECTRODES CONTAINING RESPECTIVELY NH_4VO_5, H_2MoO_4, WO_3, CuO, NO_3Ag, Al_2O_3, $SnCl_2.H_2O$, As_2O_3, $UO_2(NO_3)_2.6H_2O$, WHICH WERE CONNECTED TO POSITIVE OR NEGATIVE POLE.

not) to the negative pole of the generator have more fluidity in their liquid state than those obtained by connecting the same electrodes to the positive pole of the generator (Fig. 6) and that the deposit metals obtained by connecting to the positive terminal the electrodes coated with special compounds that are marked *a* in Table 2 bear great likeness, so far as the fluidity in liquid state is concerned, to those obtained by connecting the electrodes to the negative pole of the generator.

A New Development in Wrought Iron Manufacture

By James Aston,* Pittsburgh, Pa.

(Cleveland Meeting, September, 1929)

Three years ago the writer presented a paper on the trend of development in the wrought iron industry,[1] wherein was described a process in the development of which he has been a factor, which at that time had passed through several years of progressive experimental development but which had not then been put upon a commercial scale of operation.

The present paper deals with two years of observation and experience in the commercial operation of a plant by the A. M. Byers Co. at Warren, Ohio. It will not enter into the controversial field of the relative merit of wrought iron and steel in various classes of service, nor will it elaborate upon the characteristic services or fields of utility to which wrought iron is particularly adapted. It is sufficient to state that the wrought iron industry is upon a substantial basis and that the material finds service in pipe, where its advantages are in superior corrosion, fatigue, welding and threading qualities; in bar iron for staybolts, engine bolts, and rivets, demanding maximum service against corrosion and fatigue; in plates for corrosion service; and in chains, because of welding and shock-resisting characteristics. In short, ability to withstand the stresses of shock and vibration, or the ravages of corrosion, to hold protective coatings, and to give maximum efficiency in welding, are its features of relative superiority.

If these features were not well recognized, the wrought iron industry would have shrunk to insignificance in the face of high costs and acknowledged limitations in manufacture. To charge that this industry is built upon a structure of assumption, psychology, and improperly weighed evidence is an impeachment of the integrity or belittling of the powers of observation of users through many centuries of service experiences.

In a history which extends to prehistoric time, and which is linked up with the earliest records of ferrous products, the dominant method of manufacture, as we have known it for little over a century, occupies a very small niche in the span of years that mark production and use of wrought iron. Puddling, the outstanding manufacturing method of

* Professor of Mining and Metallurgy, Carnegie Institute of Technology.

[1] J. Aston: Trend of Development in the Wrought Iron Industry. A. I. M. E. *Pamphlet* No. 1595C (1926).

recent years, was the invention of Henry Cort in England in 1784. Improvements by Hall in 1830 put it upon a basis which has come down to the present substantially without fundamental changes in principle or practice.

Process of Making Wrought Iron

Wrought iron manufacture of today is usually associated with hand puddling. The essential steps in the process are:

1. Melting down the charge of pig iron.
2. Refining the metal to a low content of the several metalloids.
3. Disintegration of or "graining" the mass in the slag bath resulting from refining.
4. Balling up the metallic mass and thereby incorporating with it a portion of the slag.
5. Compacting the composite mass with ejection of surplus slag.

The operation requires skill and severe manual effort, with an accompaniment of small outputs and high costs of manufacture. The following description is quoted from the previous paper:

> The general furnace today is a simple reverberatory, coal-fired, and sometimes with a waste heat boiler in the stack. In the Pittsburgh district the single furnace is used, with a charge of about 600 lb. It is manned by two puddlers. In the East, double furnaces are the rule. These really are two single furnaces back to back, with the back walls removed to make a single hearth, and with one stack. The charge of 1200 to 1300 lb. is worked by four men, two at each side. The furnaces have a cinder bottom, and are lined with plastic iron ore. The charge is cold pig iron, and requires about 1¾ hr. for completion. Five heats constitute a turn, with a man-turn output of about 1400 to 1500 lb.
>
> The furnace temperature is about 2600° F., which is ample to fuse the metal initially, to fuse the slag throughout the heat, and to furnish a welding heat; but it is not enough to fuse the metal in the later stages of refining. The result of the puddling operation is the formation of a spongy mass of metal, thoroughly impregnated with liquid slag. The product is taken from the furnace as "balls" of about 200 to 300 lb. in weight. These are put through a squeezer to eject surplus slag, and form a bloom which is rolled to a rough, flat bar section called muck bar. The muck bar is sheared to short lengths, piled, heated to welding and rolled to desired sections. This "piling" operation is required to obtain the needed work upon the relatively small mass of the initial bloom. For some commodities piling and rolling are repeated; the product being then classed as "double refined" in distinction to the "single refining" of the first mentioned procedure. All products show the well-known fibrous fracture and other distinctive characteristics of wrought iron.

It is to be expected that human ingenuity has been requisitioned to increase output and minimize manual labor. Numerous so-called "mechanical puddling" processes have been devised, with a dominance of failures, but with a few attaining a commendable degree of success.

In general, the methods have employed furnaces of a rotary or oscillatory type, with the focus of attention upon obtaining agitation of the charge in simulation of the manual effort of the puddler.

Any successful method to displace hand puddling in the production of wrought iron must maintain or improve upon the characteristics of product obtained in hand puddling; it must do this with increased unit masses and aggregate output; and it must decrease manufacturing costs to an extent proportional to the expected expansion of the market for the product. Failures have been in part due to inconsistencies in quality of material produced, in part to difficulties of maintenance of equipment, and in part to manufacturing costs which, in comparison with those of hand puddling, were not attractive to capital. Metallurgically, disintegration of the refined base metal to secure minute and uniform intermingling with the slag is the crux of the problem, and was the focus of attention in the development of the Byers New Process.

Plant and Operation at Warren

Operation began at Warren in July, 1927. After a few months on a moderate scale, in which there was an ironing out of some of the mechanical difficulties which are always an accompaniment of a new project, production was put upon a regular and steadily increasing basis. Today, with some extensions of the original equipment, output is in excess of 200 gross tons per day, with operations on two-turn, six-day week program.

The process is divisible into several steps, which correspond to and parallel the major subdivisions of the hand puddling method. The plant consists of several units, each of which is adapted to efficiently carry out its special phase of the integrated operation. The several subdivisions and functions, and important features and accomplishments, are as follows:

Melting

Bessemer grade pig iron is melted in a 12-ft. dia. cupola of standard "steelworks" type; that is, similar to those used in supplying metal to Bessemer plants when direct blast-furnace metal is not available. It has a melting capacity of about 15 tons per hour, and operates continuously for a week, after which patching of the lining in the tuyere zone is necessary. The cupola is mechanically charged, necessitating therefore a minimum of labor for its operation. As is characteristic of cupola melting, there is a pickup of 4 to 5 points of sulfur; however, it is adequately eliminated by the use of about 20 lb. per ton of soda ash, added to the ladle on tapping. The full requirement for each heat is tapped at one time, then taken in a ladle to the converter house by an overhead crane.

Refining

Refining is done in two 2-ton side-blown acid-lined converters, operating on a cycle of about 25 min. for each vessel. The metal is blown "full" with an analysis when teemed averaging C, 0.06; Mn, 0.03; P, 0.10; Si, 0.02; S, 0.05. In contrast with Bessemer steel practice, no additions are made to the ladle metal, and it is important to also bear in mind in such comparison that the ladle metal in the new process operation is merely a semifinished material which subsequently undergoes completion of metalloid removal, and the important functions of degasification and deoxidation during the reactions involved in processing. The Bessemer converter is admirably adapted to the refining stage of the operation, with the important adjunct of a virtually continuous supply of metal in batches of moderate size on a relatively brief, steady cycle.

Slag Preparation

The slag incorporated in wrought iron is essentially a ferrous silicate high in iron oxide content. In hand puddling practice it is a combination of oxides resulting from the reactions of refining, with such additional ingredients as may result from a fluxing of materials from the furnace hearth. It will vary somewhat, for good or evil in results, with the nature of the charge material, individualism in practice, and character of furnace materials. A typical composition is FeO, 70 to 75 per cent.; Fe_2O_3, 5 to 10; SiO_2, 10 to 12; MnO, 2; Al_2O_3, 2; P_2O_5, 2; and occasional or small amounts of CaO, MgO, or other oxides. The iron silicate is the important or dominant ingredient, with the others secondary or merely incidental.

In the new process, preparation of the slag consists of independent melting of the constituent ingredients in the proportions for the desired composition. Puddling-furnace tap cinder (where available), heating-furnace cinder, roll scale, iron ore, and sand represent available sources of supply. The composition is maintained in close conformity to the slag found in good wrought iron, with adjustments in line with experience which has shown that improved characteristics of product may be obtained.

The melting is done in a tilting regenerative open-hearth furnace, oil fired, of 20-ton steel rating. It is of standard type, magnesite lined, but with additional water cooling to protect the hearth from the heavy scouring action of the molten slag. Make up slag is transferred in a ladle to the processing floor as required.

Disintegration

As noted heretofore in the general discussion, disintegration of the metallic mass is the dominant feature in the manufacture of wrought iron,

in order that a sponge shall be formed to serve as a carrier of the slag, which must be incorporated with the base metal. A description of this phase of the new process operation is of especial interest, not alone because of its fundamental importance and the method by which it is accomplished, but because it probably represents the first recognition of the dominance of this feature and a consequent concentration of effort in devising effective means of comminution. It is the keystone of the new process, and the existing scheme of operation is illustrated in the accompanying photographs.

FIG. 1.—SUPPLYING SLAG TO THIMBLE.

The operation is carried out in a set of unlined, stationary cups or thimbles, resting upon standards along the pouring platform. The average heat of blown metal is about 5000 lb., and this is as a rule formed into two balls; for which plan two cups are employed. The cups are rectangular, roughly 3 by 4 ft. in bottom dimensions, and 5 ft. deep; with considerable taper to the top. One of the cups carries about 2½ to 3 ft. depth of slag, brought on as needed from the melting furnace, and illustrated in Fig. 1. Into this slag, one-half (about 2500 lb.) of the ladle of blown metal is poured in a steady stream over the lip, shown in Fig. 2.

The weight and rate of pouring are under observation on the crane scale from which the ladle is suspended. The average pouring time is about 3 min., being equivalent to a 1 to 1½-in. nozzle stream.

During pouring, there is marked churning and agitation of the slag, with a boiling action causing it to rise to the top of the cup; but there is no violence in the observable reactions. From time to time moderate amounts of cold granulated slag are shoveled into the cups during pouring, largely for the purpose of quieting a too vigorous boil, which might cause the rising slag to flow over the rim of the vessel.

FIG. 2.—POURING THE METAL.

Immediately upon completion of the pour, the boil subsides and the slag level goes down markedly. The cup is picked up with the crane, and the excess slag (Fig. 3) is poured into the adjoining empty vessel, which is then ready to receive the remaining half of the ladle metal. The decanted cup now contains the solidified, spongy mass of metal, intermingled with liquid slag, conforming in all respects to the product of the best hand puddling practice. The "ball" is dumped upon a carriage, illustrated in Fig. 4, and transferred to a hydraulic press to be compacted into a bloom. Naturally, the slag take-up of the ball necessitates a make-up supply to the cups from time to time, as indicated by the level of slag in the vessels, the general requirement with present practice approximating 600 lb.

per ton of wrought iron produced. It must be realized, however, that the slag material make-up is very much less than the melting make-up, since the greater part of ball take-up is recovered after squeezing.

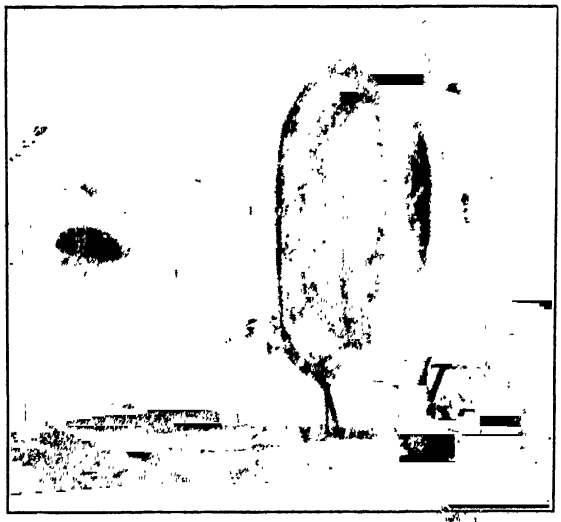


FIG. 3.—POURING OFF THE SLAG.

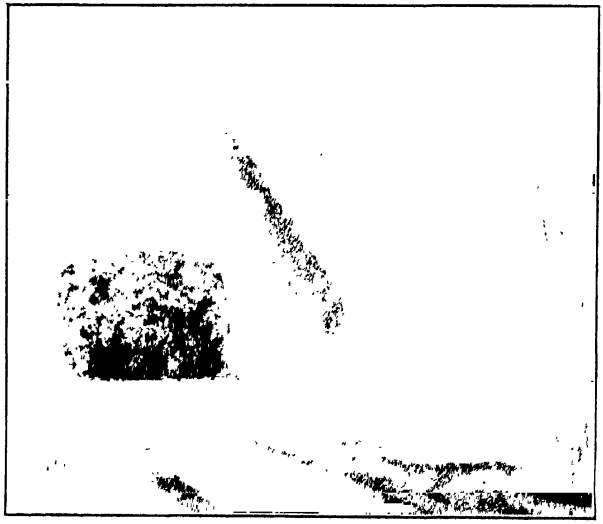


FIG. 4.—DUMPING THE BALL.

The "ball," which is at a welding heat, is compacted to a solid, rectangular bloom about 12 by 14 in. by 5 ft., in a manipulator type hydraulic press, and is immediately sent to a 29-in. three-high blooming mill, where it is roughed down to appropriate sizes. On the same heat, additional rolling in a 24-in. three-high mill produces the shipping prod-

uct, either billets suitable for direct rolling to skelp, or standard muck-bar sections used for piling. A steadily increasing proportion of the output is in billet form.

Fundamental Principle

The simplicity, positiveness, and smoothness of the operation is a matter of general comment by the observer, followed almost immediately by the query, "How does it happen?" It is appropriate, therefore, to turn from the description of plant and operation to an explanation of the principles upon which the process is based. While operations are simple, they are built upon fundamental physicochemical principles which are incontrovertible.

Refining of the base metal and the preparation and melting of the slag need no explanation. The mechanical admixture of base metal and slag is the crux of the situation. The execution is most effective if one is solid and the other liquid; preferably a solidification of the iron, because of its higher fusion point and preponderant volume in the product. The metal is poured at a temperature in excess of its fusion point of 2750° F., while the slag, liquid at all stages of the operation, has a general working temperature of about 2300° to 2400° F. Under present operating conditions, the slag volume relative to metal poured into the cup is 6 or 8 to 1. This is considerably in excess of the quantity needed to absorb the heat of solidification of the metal, without becoming superheated to a temperature above or dangerously near the fusion point of the iron. With these conditions, therefore, the slag is an active quenching medium which solidifies the metal promptly and continuously as it enters the bath.

Accompanying this is the all-important principle upon which the process is founded. It is a well-established fact that molten iron or steel carries large volumes of gas in solution; and that the solubility relationship becomes nil upon change of metal state from liquid to solid. The rate of gas evolution is proportional to the speed of solidification. The operating conditions of the process as described are such that the metal is shattered by the gas evolution as it solidifies. Being heavier than the slag, it settles to the bottom of the cup as a spongy mass, which coheres as a result of a welding temperature automatically maintained in the heat exchange, and which is completely intermingled with the liquid slag.

There are some interesting and important accompaniments of this operation. In view of the oxidizing and basic nature of the slag, the metalloid content of the blown metal is appreciably reduced during pouring, particularly with respect to carbon, manganese, and sulfur. In fact, with increasingly higher carbon metal, the additional gas created by reaction of carbon with the iron oxide of the slag may bring about a

violent reaction resulting in a heavy boil and overflow of a slag from the cup. And yet the seemingly paradoxical result is reached of effective deoxidation of the base metal by reason of the change of solubility of iron oxide in iron from a considerable degree to nil on change of state from liquid to solid, and the absorption of the liberated iron oxide by the slag surrounding the multitude of disintegrated particles.

Naturally, also, there is complete degasification of the base metal for similar solubility transitions; as noted above, this is the fundamental feature of the process.

Thus one has a simple physicochemical application which effectively accomplishes that which the steelmaker is struggling with through the agency of additions which tend to liberate gases or form and release inclusions prior to solidification. The steel ingot lacks the important condition furnished by the liquid slag of the process; namely, a ready path of exit for the released gases, and a contact absorbent for the liberated non-metallics.

Some Analogies and Comparisons

Long usage has linked up quality wrought iron with hand puddling. The focus of our attention was to reproduce this quality in all respects in a product having all the determinable characteristics of wrought iron. The results have measured up to the objective. The material conforms to all standards set for wrought iron—chemical, metallographic, and physical; a conclusion subscribed to by many investigators, including railroad and government representatives, after careful examination and test. This is confirmatory of our own studies in laboratory, mill and field.

In many respects, the new process product has superiority of quality. Greater uniformity results from the controllability of operations and the elimination of individualism. There is benefit in the added work put upon the larger mass. Uniformly low content of carbon in the blown metal has resulted in virtual elimination of blisters, the bane of wrought iron manufacture. Low metalloid content, and particularly the controllability and adjustability of metal and slag character independently, has benefited the welding and other physical properties of the product. In addition, this operating advantage points the way to the manufacture of wrought iron of special characteristics and adaptability, including the possibility of entry into the alloy field.

It is almost needless to point out the advantages accruing from the general parallelism to steelworks' practice in equipment, personnel, and operating procedure. Tonnages of individual blooms and in the aggregate are a matter largely of engineering expediency. The all important item of lowered costs of manufacture is an accompaniment. In com-

parison with steel manufacture, the new process has certain special features which add to the cost, but they are or may be largely offset by such items as additions, molds, soaking pit charges, and cropping, which enter into the cost of steel production.

While the concentration of effort in the development was upon the production of quality wrought iron without thought of process involved, it is interesting to note the exact parallelism of the new process to the reactions and accomplishments of hand puddling. Melting, refining, and slag formation involve identical fundamental principles and reactions and need no elaboration. The "opening" or "graining" of the iron as it "comes to nature" has been generally conceded as the special art of the puddler and a stumbling block in the development of mechanical puddlers. It is a misconception that disintegration is the direct result of physical effort of the man or machine; in the case of the latter, the tendency is rather towards agglomeration that disintegration. Disintegration in these operations is the result of degasification on solidification of the iron as its fusion point passes the operating temperature of the furnace when the metal nears the end point in carbon elimination. Effort is necessary primarily in an attempt to bring all portions of the refining mass into the favorable zones of reaction, as contrasted with the unfavorable conditions of relatively cold interiors or furnace bottoms. The physicochemical forces of reaction are identical; except that in the new process they are more effective and more uniformly executed, due to the more favorable operating condition of approaching the reaction or solidification from above with a fully and uniformly refined iron, rather than rising into the solidification range with a progressively and irregularly refined metal. The new process may be classed as puddling in the logical interpretation of reactions and accomplishments.

The Future

The Warren operation is serving a useful purpose as a proving ground. Construction is well under way on a new plant being erected by the A. M. Byers Co. at Economy, Pa., in the Pittsburgh district. The Bessemer converters, bottom blown, will be of 10 tons capacity, and the balls produced will be about 2 tons in weight. A more rapid operation will be obtained by a cup-car system of handling, with progressive movement of the cars to the several zones. Initial production will be 600 gross tons per day, with only minor extensions to double or treble this output. Immediate mill equipment will be blooming, plate, bar, and skelp mills; with projected extensions to include blast furnace and coke oven plant and finishing mills. This project should put wrought iron into its proper place in the field of ferrous products, through an expanding market made possible by lowered costs, greater tonnages, and diversification of output.

DISCUSSION

G. B. WATERHOUSE, Cambridge, Mass.—Are the 10-ton converters to be bottom blown?

J. ASTON.—They are bottom blown.

G. B. WATERHOUSE.—Do you plan to use cupola melting?

J. ASTON.—For the time being. The Ambridge plant has provision for blast furnaces, but not for the operation that will start early next year. That operation will have cupolas for melting, two 10-ton converters, a blooming mill, a universal plate mill, a bar mill, and a skelp mill.

MEMBER.—Does the height of the metal ladle above the slag thimble have any bearing on the formation of the sponge?

J. ASTON.—Very probably not. The average height of pour from the ladle to the surface of the metal is 6 to 8 ft. That is merely a matter of convenience, however. We have poured from heights varying from 1 ft. to 20 ft., without material differences in effects. We used to think that height had a bearing, but we are now convinced that it is quite secondary.

H. D. HIBBARD, Plainfield, N. J. (written discussion).—The author and A. M. Byers Co. are to be commended for their persistent efforts and progress made through many obstacles to the point they have now reached. The product they get, however, is not puddled iron though it may perhaps properly be called wrought iron, which has been made in many ways. Whether or not Aston iron will meet all the requirements of puddled iron may take years to demonstrate, particularly as regards resistance to corrosion. Some puddled iron exposed to the weather lasts for a generation or more.

The technique of the Aston process differs enough from that of the puddling process to raise some questions. However closely the composition of the slag approaches that of puddle cinder, the difference in length of time the two are in contact with the iron, and the different conditions of their contacts may conceivably lead to differences in the products.

Blown Bessemer iron is usually in this country a redshort material. To make it into steel sufficiently free from redshortness, manganese is added, and several minutes—usually too short a period—then elapse before teeming, in which time chemical reactions take place, and the nonmetallic, insoluble products thereof escape more or less completely from the metal.

In the Aston process no chemical purification of the blown iron is claimed to be effected by the slag. Its admixture with the metal is almost instantaneous, or at most takes but a few seconds, while in the puddling process their contact and mixing lasts some minutes even after the iron has come to nature. Will the Aston process in the brief period allowed, change redshort blown iron into good metal, good in all respects?

It is argued that since all wrought iron contains slag, slag is a beneficial and even essential ingredient. But the argument suggests the fable of the rat that had lost its tail. It is making a virtue of a necessity. It may safely be maintained that the less slag there is in iron, the better the quality. Swedish iron, which is the best, has the least. Slag being however unavoidable in wrought iron it is most desirable that what there is be evenly distributed in small particles or stringers throughout the metal, as the larger the masses, and the more uneven their distribution, the more harm they do to the quality.

J. ASTON.—Of course, the question as to whether or not it is puddled iron depends entirely upon our definition of puddling. If we define puddling as an operation

carried out in a distinctive type of equipment by a certain manual effort, of course it is not puddling. If we define puddling as a sequence of characteristic operations accomplishing a certain result, it is puddling. I will not attempt to answer the question now, because it is a matter of dispute; and it is being discussed before the technical committees of the American Society for Testing Materials, in an attempt to reach a solution of the whole question, since it enters into the question of specifications. It is a point of view entirely, and as a matter of fact, we have no exact definition of puddling at the present time. It is generally associated with equipment rather than with a process, which is probably the wrong point of view.

With regard to the quality of the product, as relates to corrosion, one speaks in terms of the life of a man as a rule, and commercial operations can not await such a verdict.

No one can answer the question, "Will it do all that has been done by the hand-puddled iron?" Time alone will tell the story. The only answer thus far is that so far as our investigations have gone, and so far as the investigations of independent authorities have gone, in every way we can put it to test, and in every way that we can examine its characteristics, and in all that makes up the sequence of reactions, it is entirely in conformity with the highest standards set for wrought iron.

F. B. RICHARDS, Cleveland, Ohio.—Do you get staybolt iron direct without repiling?

J. ASTON.—We have made staybolt iron by direct rolling from billets, and it has conformed to the general standard tests for staybolt material; but I would not at this time go on record as stating that wrought iron of double refined quality may be regularly made by direct rolling from a billet. Experiments along this line are in progress.

F. B. RICHARDS.—Microscopic tests have shown it uniform.

J. ASTON.—The uniformity and the freedom from large slag pockets are decided advantages of the method. The disintegration is more uniform than in hand puddling.

F. B. RICHARDS.—Is it true that the more slag you get out, the better product you have?

J. ASTON.—It depends on what the material is to be used for. Where physical properties are dominant, slag in quantity is not desirable, especially in large pockets or coarse distribution. On the contrary, if we accept the general theory that wrought iron owes its qualities to the incorporation of slag, and are concerned with corrosion resistance, a greater amount of slag is desirable than where strength requirements are uppermost.

F. B. RICHARDS.—That is what I thought.

J. ASTON.—Some of Mr. Hibbard's comments are too speculative and too involved to be answered at this time. Taking issue with Mr. Hibbard, we claim and mention that the metalloid content is materially reduced with respect to carbon, manganese and sulfur. In addition, the vital feature of removal of oxide and gas is accomplished in an important degree.

With regard to blown Bessemer metal and its redshortness, one must bear in mind—and it was distinctly stated in the paper—that the blown metal is only a halfway stage to the end point; and that the physicochemical reactions of the process accomplish purification, deoxidation and degasification, which in steel making result from additions to the ladle metal.

F. B. RICHARDS.—What about the composition of the slag?

J. ASTON.—In present practice the slag carries between 10 and 12 per cent. SiO_2. That is somewhat lower than a characteristic hand-puddling tap cinder. The exact composition of the slag of the hand-puddled ball is difficult to determine.

In the course of our experiences we have found that high SiO_2 in the slag causes poor welding quality in the product. Present standards are the result of such observation and experience.

C. H. HERTY, JR., Pittsburgh, Pa.—Mr. Hibbard said that the larger the amount of slag, the poorer the metal, and the important thing that Mr. Hibbard forgot was the kind of slag used in the metal. Last year and the year before last we made a series of studies of the effect of different types of slags in metal on the forging qualities of steel, and for the first series we took heavily oxidized metal, and deoxidized progressively in different ingots with silica. The first ingot had no silicate, only iron oxide. In the next ingot the iron silicate was very low, and in the next one it was increased, and gradually when we got to killed steel, we had included in the metal almost pure silica. Upon forging, we found that there were only two ingots that would forge down properly, and the analysis of the silicates of those two ingots was very similar to that of wrought iron slag. Above or below a certain composition, redshortness begins in the metal.

Mr. Hibbard brought up the refinement of the metal. I think Dr. Aston has overlooked it in the explanation of the fundamental principle of the process. If you take a test piece out of an open-hearth furnace and allow it to solidify in the mold in the usual way, you will find that the carbon content is from 1 to 3 points lower. The reason for that drop is the evolution of CO from the mold; we have gotten fairly definite information that the CO comes from a reaction between the carbon and the iron oxide in the metal, and not from a residual gas in the metal. If we drop 2 points of carbon, it is equivalent to about 3 points of oxygen. This makes all of the difference whether a piece is going to be redshort or forge perfectly. I think that is probably one of the principal reasons for the effect of rapid shotting. There is a violent evolution of gas caused by the carbon-iron oxide reaction. In the second place it is the type of slag, not the quantity of slag that counts.

J. ASTON.—Confirming Dr. Herty's remarks, the type of slag is exceedingly important; fully as much as metal characteristics.

Unreduced Oxides in Pig Iron and Their Elimination in the Basic Open-hearth Furnace*

By C. H. Herty, Jr.† and J. M. Gaines, Jr.,‡ Pittsburgh, Pa.

(New York Meeting, February, 1929)

During the past few years frequent reference has been made to a certain type of iron known generally as "bad iron," "dirty iron," etc., both by steelmakers and producers of iron castings.[1] Open-hearth operators have claimed that such iron was entirely within the specified limits as to ordinary analysis but it was difficult to make good steel from it. It has been suggested that unreduced material in the iron is responsible, also that most trouble is experienced with the iron when the blast furnace is delivering a product whose analysis is more or less variable. Other reasons suggested are the use of scrap or borings, unsintered flue dust in the burden, a cold hearth, too high a proportion of unsuitable grade of ore, or the form of the carbon in the iron.

Accordingly, a subcommittee was appointed at the fall meeting of the Open-hearth Committee of the American Institute of Mining and Metallurgical Engineers held in Pittsburgh in October, 1926, to investigate the reasons for the occurrence of this bad iron and suggest methods for preventing its appearance. This committee enlisted the cooperation of the U. S. Bureau of Mines Experiment Station at Pittsburgh in undertaking a study of pig-iron quality as affecting the open hearth. The following is a report of the findings to date:

Method of Testing

Inasmuch as a "spell" of dirty iron occurs without warning and may be of short duration, it was deemed advisable to attempt to simulate the conditions existing before and during such a period and compare the quality of the steel made with the normal and with the dirty iron. The Bourne-Fuller Co., of Cleveland, which has a single furnace that supplies

---

* Published by permission of the Director, U. S. Bureau of Mines.

† Physical Chemist, Pittsburgh Experiment Station.

‡ Assistant Physical Chemist, Pittsburgh Experiment Station.

[1] R. L. Cain: The Manufacture of Forging Steel by the Basic Open-hearth Process. A. S. M. E. Pamphlet No. 1591-C (1926).

Round Table Conference on "Blast-furnace Operations and the Character of Pig Iron and Castings," joint meeting Iron and Steel Committee, A. I. M. E., and American Foundrymen's Assn., Feb., 1928. For minutes, see Iron and Steel Technology in 1928, A. I. M. E, 334.

metal direct to the open-hearth shop, offered to cooperate in such a test. Three heats were observed using iron made under normal operating conditions at the blast furnace. The burden was then increased to throw the furnace on the cold side and two open-hearth heats were made from the resultant low-silicon, cold-hearth iron. The operation of the blast furnace and open hearth was followed closely, a large number of samples, temperature readings and other data being taken. The open-hearth product, a low-carbon rimming steel, was rolled into 4 by 4-in. billets, then to 1½-in. rounds; some of the billets were rolled into sheets and were zinc-coated.

All of the samples were analyzed for the usual constituents as well as for non-metallic inclusions, and billet samples from each heat were analyzed for iron oxide.

Summary of Results

Blast Furnace.—It can be stated from the results that there is generally a certain quantity of oxides, chiefly SiO_2, FeO, MnO and Al_2O_3, in pig iron from the blast furnace. The total amount varied in this test from a trace to about 0.13 per cent. of the weight of the iron. It will be shown that the highest percentages of silicates (this term will be used to indicate the total non-metallic impurity since SiO_2 is the main constituent) are met at times when the furnace is working irregularly. A comparatively rapid change in hearth temperature, whether hotter or colder, or an increase in the rate of stock descent, such as a slip, will cause a sharp increase in the silicate content of the iron.

Open Hearth.—The iron used during the five heats varied in its silicon content from 1.11 to 0.20 per cent. As would be expected, the heats with the low-silicon iron melted soft and offered some difficulty in working and in shaping the slag; however, no noticeable difference in the quality of the finished steel could be detected. Bars from the heats were rolled into sheet and were zinc-coated, with no difference in quality between heats. It should be kept in mind that low-carbon rimming steel heats were made in this investigation in order to avoid complications arising from the introduction of silicon in higher carbon heats.

Blast-furnace Operation

Samples of slag and metal were obtained from each cast, including No. 2117 through 2142. In addition, during the period of casts 2129 through 2142, a detailed log sheet was kept in which was recorded the temperatures of slag, metal and four of the nine tuyeres, the pressure and temperature of the blast and top gas, as well as notes on the appearance of slag, metal and tuyeres. A condensed form of this log is given herewith.

CONDENSED LOG SHEET OF BLAST-FURNACE OPERATION

Jan. 26, 1927

7:00 a.m.	Cast No. 2128. Si, 1.32 per cent.; S, 0.024 per cent.
9:30	Flush slags bluish and brittle.
10:02	Cast No. 2129. Si, 1.47 per cent.; S, 0.025 per cent.
1:10 p.m.	All cold wind on.
1:35	Cast No. 2130. Si, 1.23 per cent.; S, 0.029 per cent.
2:30	Hanging slightly. Cold wind off.
3:30	Cold wind on.
5:00	Cast No. 2131. Si, 1.35 per cent.; S, 0.026 per cent.
5:30	One-fourth cold wind on. Increased rate of blowing.
6:30	Add 200 lb. ore to burden. All cold wind.
7:40	Furnace begins to hang a little. Flush slags are limy but still hot.
7:57	Cast No. 2132. Si, 0.79 per cent.; S, 0.039 per cent. Metal still fairly hot. All cold wind off.
8:56	Decreased rate of blowing by one revolution.
9:35	Add 600 lb. ore to burden. Total burden is now 11,800 lb. per round.
11:30	Cast No. 2133. Si, 0.73 per cent.; S, 0.026 per cent.

Jan. 27, 1927

1:00 a.m.	Cut one more revolution. No. 1 tuyere looking sluggish.
3:05	Cast No. 2134. Si, 0.85 per cent. S, 0.025 per cent.
3:50	All front tuyeres show signs of trouble.
4:05	Furnace starts to hang. Much cold stock in bottom.
4:30	Top pressure lower. Blowing slower.
4:45	Slipped during flush.
6:40	Cast No. 2135. Si, 1.08 per cent.; S, 0.025 per cent.
7:00	Not making much gas. Stoves getting cold.
9:30	Flush slag shows brown color. Most of tuyeres are blocked.
10:00	Cast No. 2136. Si, 0.65 per cent.; S, 0.037 per cent. All cold wind on.
10:35	Left side of furnace is cold. Slight slip.
11:55	No cinder at flush.
12:20 p.m.	No cinder. Furnace still taking 4 rounds per hour.
12:25	Small amount of very black cinder.
12:50	Hanging in shaft; slipped. One half cold blast on.
1:30	Cast No. 2137. Si, 0.38 per cent.; S, 0.062 per cent. All cold blast off.
3:50	Flush slag is cold and yellowish.
4:30	Take off 1400 lb. ore. All stoves on regular schedule. Three skips of coke.
5:00	Cast No. 2138. Si, 0.27 per cent.; S, 0.072 per cent.
6:25	No flush cinder. Furnace has been hanging since cast.
6:35	Checked. Moved down nicely.
8:00	Cast No. 2139. Si, 0.34 per cent.; S, 0.053 per cent. Slag limy and thick. Tuyeres look a little hotter.
8:45	Stopped charging. Furnace hanging badly. Checking does not help. All tuyeres blocked.
10:40	Still hanging. No cinder from monkey. Top pressure zero.
11:15	Cast No. 2140. Si, 0.27 per cent.; S, 0.036 per cent. Made half ladle of iron. After cast tuyeres look better.
11:35	Stopped one engine. Blast pressure still high.

Jan. 28, 1927

12:55 a.m. Blast pressure lower. Started second engine. Tuyeres are opening up.

1:15 Checked. Moved out of reach.

2:15 Flush slag is thick, brown and limy.

3:18 Cast No. 2141. Si, 0.53 per cent.; S, 0.027 per cent. Hangs right after cast.

5:00 Reduced speed of engines. Hanging badly. Tuyeres blocked. Moves off on checking.

6:05 Tuyeres hotter. No cinder from monkey.

6:45 Cast No. 2142. Si, 0.77 per cent.; S, 0.021 per cent. Settles after cast and action aut tyeres begins. Slag gray.

Fig. 1 shows graphically the variation in temperature of tuyeres and iron with the changes in the percentages of sulfur, silicon, and silicates in the metal during the period from cast No. 2129 to No. 2142. It will be observed that until No. 2135 there appear to be no striking changes taking place. At this point the temperatures begin to fall rather rapidly and there is a drop in silicon accompanied by a rise in sulfur and in silicates. At No. 2137 the temperature of the tuyeres is seen to be rising and by the following cast it has made itself felt. The analysis of the iron is beginning to return to normal and its temperature appears to be rising. The loosening effect of the higher hearth temperature is probably the cause of the irregularity which follows cast No. 2139. Although the sulfur continues to drop, the silicon and metal temperature do not rise. It is significant that the furnace made only 13.6 tons of iron on cast No. 2140, in contrast to 27.8 tons on the previous cast and a normal produc-

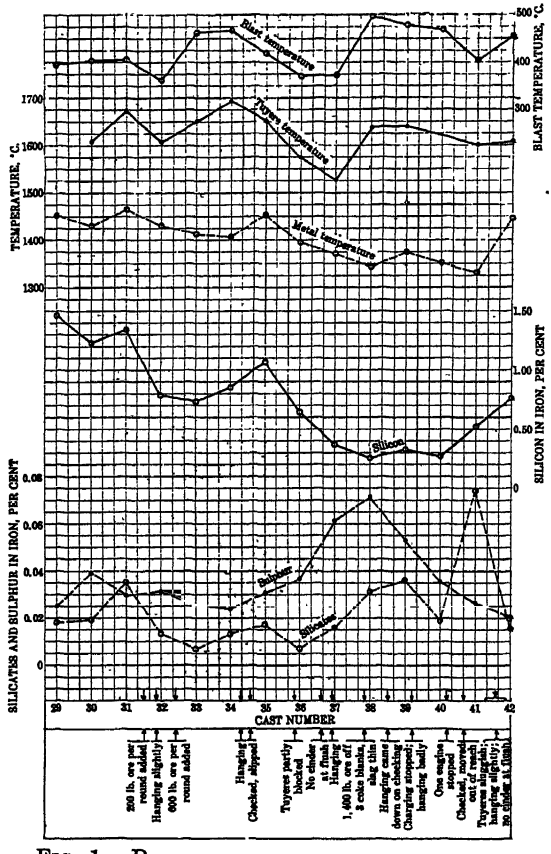


FIG. 1.—RECORD OF BLAST-FURNACE OPERATION, BOURNE-FULLER CO., JAN. 26–28, 1927.

tion of 45 to 50 tons. This may be taken to indicate that low-sulfur iron can be produced at low temperature if it is made slowly, but normal temperature is essential for normal silicon content.

Soon after cast No. 2139 the furnace hung, all of the tuyeres became blocked, and it became necessary to stop charging. The retarded action of the stock is probably responsible for the drop in silicates observed with cast No. 2140. Shortly after cast the cinder notch was opened and the blast cut off. This caused a definite slip, and a marked increase in the silicate content of the iron on the following cast due, probably, to the introduction of much cold stock, or scaffold, into the iron in the hearth.

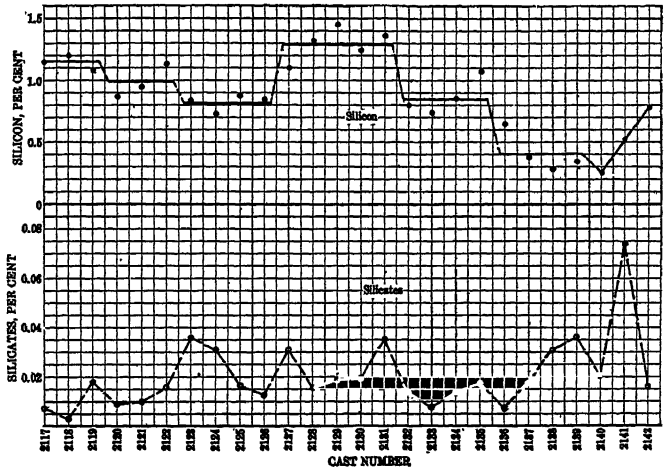


FIG. 2.—VARIATION IN SILICON AND SILICATES ON CASTS NOS. 2117 TO 2142, INCLUSIVE.

The effect of irregularities in the furnace working on the silicates in the pig is better illustrated by Fig. 2. This shows the percentages of silicon and silicate in the iron from casts No. 2117 through No. 2142. The figures for silicon have been averaged in several groups, each one representing fairly uniform operation, as shown by the small variation in the silicon content. The average for each group is shown by a heavy horizontal line on the plot. It will be noticed at once that wherever the heavy line breaks—that is, when the furnace shifts, for example, from making an average of 0.81 per cent. silicon to one of 1.29 per cent., there is a sharp rise in the percentage of silicates, shown on the lower curve. As soon as the furnace operation becomes fairly steady at the new silicon figure, a decrease in silicates takes place. If now a fairly rapid and considerable drop in silicon takes place, the percentage of silicates will rise.

Fig. 3 has been included to show that there is a qualitative relation existing between the amount of silicates in the iron and the variability of the silicon content. This has been brought out by plotting the per-

centage of silicates against the ratio of the change in silicon from the previous cast to the average silicon for the cast in question and the previous one. For example; for a change from 1.20 to 1.00 per cent. silicon, the ratio would be

$$\frac{1.20 - 1.00}{\frac{1}{2}(1.20 + 1.00)} = \frac{0.20}{1.10} = 0.18.$$

Every cast from which samples were taken, No. 2117 through No. 2142, has been included in Fig. 3. During the latter part of the test,

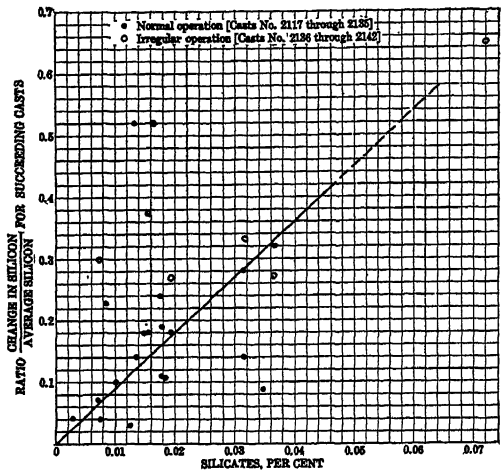


FIG. 3.—RELATION OF SILICATE CONTENT TO VARIATION IN SILICON.

when the furnace was making iron slowly and in general feeling the effect of the abnormal burden, it was found that the quantity of silicates for a given ratio was less than for normal operation. These seven casts (2136 to 2142) have therefore been indicated by open circles, the remainder being shown by solid circles. It is significant that two of these represent periods when a definite slip occurred; the other five were periods of hanging. The latter all fall above the line on Fig. 3, whereas of the two former, one is on the line and one is below. This is in accord with the general expectation that slipping is more dangerous than hanging from the standpoint of silicates.

The fact, mentioned above, that changes in silicon during periods of low iron production are accompanied by the introduction of fewer inclusions into the iron than like changes under normal operation, emphasizes the physical nature of the process. During the irregular period, production is slowed considerably and consequently less cold stock is carried down into the hearth. Furthermore, more time is probably available for reduction of the oxides in the hearth than when the furnace is operating at a normal rate.

In general, Fig. 3 shows that although major irregularities do give rise to an abnormally dirty iron, smaller variations are accompanied by correspondingly small amounts of silicate in the metal. The distinction, therefore, between good and bad iron is probably one of degree. The dividing line, or tolerant limit on silicates, will depend upon the particular conditions under which the iron is used.

Nature of Silicates

Determination of the silicate content of the iron was carried out by a method described by Dickenson,[2] in which the iron is dissolved in cold 10 per cent. nitric acid, leaving the silicates unattacked. The residue is treated with hydrochloric acid and sodium hydrate to remove ferric nitrate and silicic acid. Owing to the large amount of graphite in the residue the latter must be ignited to constant weight, leaving only the silicates behind. This is then weighed, examined, and analyzed.

Seen under the microscope or binoculars the inclusions from the pig iron show two main types of particles: The first are all nearly pure SiO_2, having a wide variety of shapes and sizes; in general, the particles of silica are roughly spherical. Occasionally, a perfect sphere is seen, indicating previous existence as a liquid. More usually the particles are rough, with an irregular contour. The same type of particle has been observed in iron ore and in samples of steel taken from the open hearth after an addition of hot metal. Glassy material, which is either white or transparent, is also to be found in a number of rather unexpected shapes—ribbons, fins, plates, or threads.

The second prevalent type of inclusion is what may best be described as a network—black spongy or lacelike clusters. These are presumably composed of other oxides. When there is fluxing between this network and a silica particle, a black, glassy substance resembling an iron or manganese silicate results. The network generally carries, adhering to it, numerous very small grains of silica.

Just what effect the ignition of the sample prior to its inspection has on its appearance is difficult to say. The fact that, after ignition, the inclusions appear mainly as discrete particles, is an indication that little change, if any, has taken place. Of course, any lower oxides such as FeO and MnO will be oxidized.

There are certain other types and colors rarely observed—such as bluish white egg-shaped particles or a brownish tinge in the network.

[2] J. H. S. Dickenson: A Note on the Distribution of Silicates in Steel Ingots. *Jnl.* Iron and Steel Inst. (1926) **1**, 177.

See also C. H. Herty, Jr., G. R. Fitterer and J. F. Eckel: A Study of the Dickenson Method for the Determination of Non-metallic Inclusions in Steel. Carnegie Inst. of Tech. *Bull.* 37 (1928).

The oxides present, in order of decreasing concentration, are SiO_2, FeO, Al_2O_3 and MnO. No trace of CaO was found in the several samples on which a determination was carried out. What other oxides may be present is not known; if there are any their amounts must be almost insignificant, because the total of the four mentioned is always close to 100 per cent., within the error of analysis. Samples for analysis weighed 0.005 to 0.20 g., the average being 0.020 gram.

Table 1 gives some typical analyses of the extracted residues:

TABLE 1.—*Typical Analyses of Silicate Residues*

Cast and Ladle Numbers	Percentage of					Percentage Silicates in Iron
	SiO_2	FeO	MnO	Al_2O_3	Total	
2130	40.5	40.5	12.3	12.3	105.6	0.0193
2131	20.4	52.6	3.4	19.1	95.5	0.0351
2135–2	49.6	32.3	2.4	18.1	102.4	0.0216
2142–2	13.3	71.6	0.8	13.2	98.9	0.1370
Average* of all determinations	47.8	28.9	9.6	14.3	100.6	0.0250

* Not including three samples on which analysis was carried out on less than 0.005 gram.

Change in Silicates in the Hot Metal between Blast Furnace and Open Hearth

One point of interest is the change in concentration of silicates and of silicon in the pig iron which takes place between the point of sampling at the blast furnace and the ladle at the open hearth. The analyses obtained from individual ladles at these two points are given in Table 2.

TABLE 2.—*Comparative Analyses of Pig Iron at Blast Furnace and Open Hearth*

Cast No.	Ladle	Silicon, Per Cent.			Silicates, Per Cent.		
		At Blast Furnace	At Open Hearth	Change	At Blast Furnace	At Open Hearth	Change
2136	1	0.66	0.66	0	0.0059	0.0305	+0.0246
	2	0.63	0.63	0	0.0087	0.0491	+0.0404
2137	1	0.38	0.31	−0.07	0.0085	0.0126	+0.0041
	2	0.37	0.35	−0.02	0.0239	0.0184	−0.0055
2138	1	0.23	0.24	+0.01	0.0291	0.0438	+0.0147
	2	0.30	0.22	−0.08	0.0338	0.0319	−0.0019
2139	1	0.36	0.20	−0.16	0.0278	0.0479	+0.0201
	2	0.32	0.20	−0.12	0.0448	0.0653	+0.0205
2140	1	0.27	0.26	−0.01	0.0197	0.0239	+0.0042

It should be remembered that these ladles were transferred direct without the intervention of a mixer.

It will be seen that of the nine ladles which were sampled at both points, six show a drop in silicon, one a slight increase, and two are unchanged. On the other hand, all except two show an increase in percentage of silicates. It is possible, of course, that these differences are due simply to the normal variation in the composition of the iron as it comes from the tap hole during any one cast. However, a more probable explanation is that the metal has been oxidized during its passage down the runners at the furnace, or in the ladle, or while pouring into the open hearth. Oxidation has resulted in the conversion of silicon to silica, and some of this silica has been removed by floating up out of the iron. The silica which is not eliminated causes the observed increase in the silicate content. It is fairly well established that liquid iron in the air is at all times covered with an oxide film, and this would certainly tend to react with dissolved silicon.

Open-hearth Heats

As already stated, five heats of soft steel were made from the pig iron produced during the test period. The first three were charged with iron

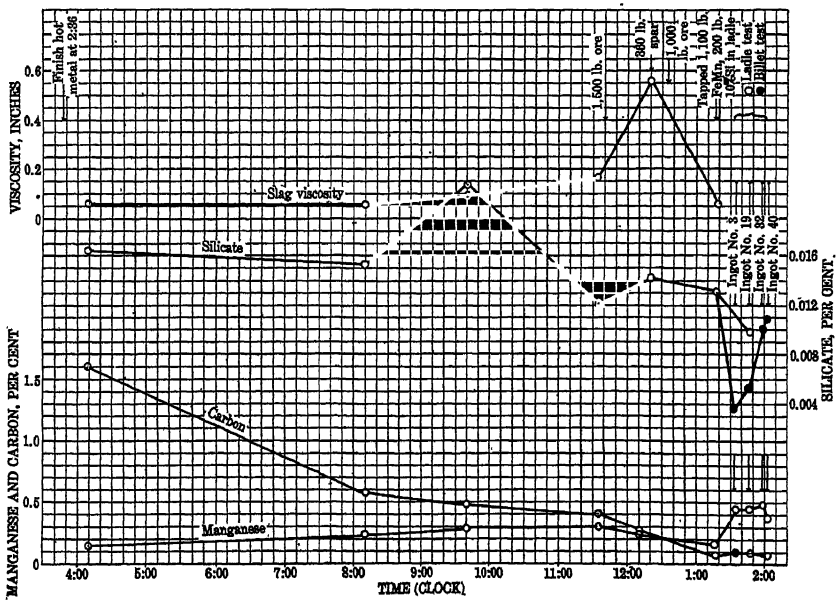


Fig. 4.—Elimination of manganese, carbon and silicates, and slag viscosity on heat No. 1 (47039).

which was supposedly normal, and the last two with iron which was made while the furnace was "off."

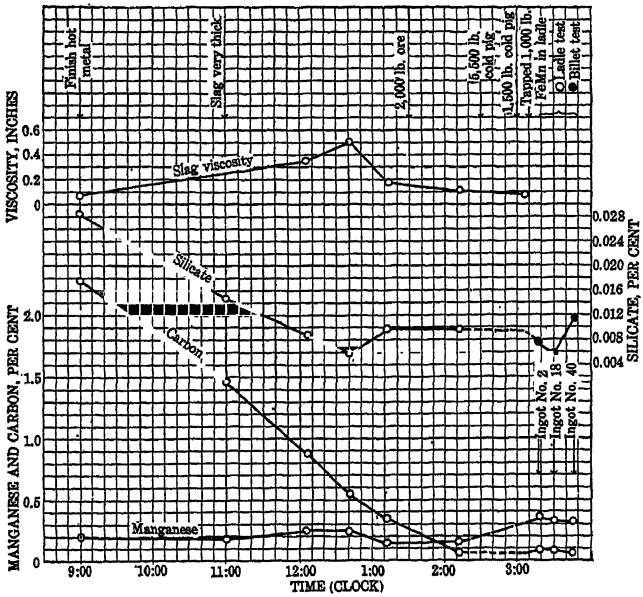


FIG. 5.—ELIMINATION OF MANGANESE, CARBON AND SILICATES, AND SLAG VISCOSITY ON HEAT No. 2 (37044).

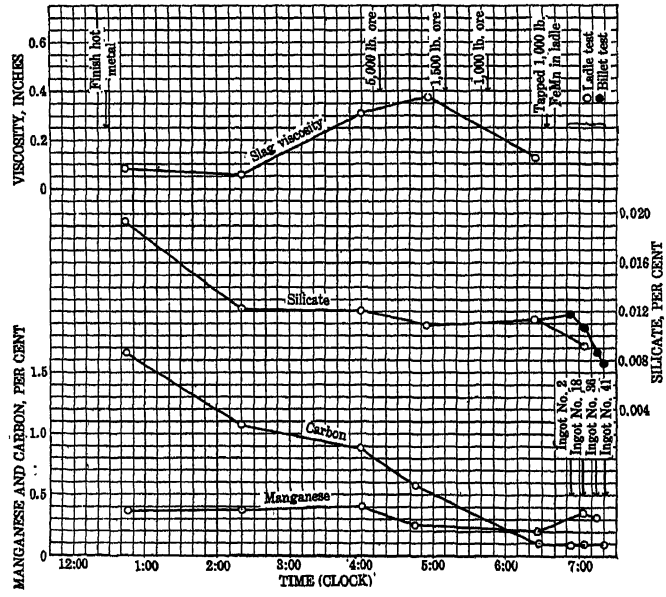


FIG. 6.—ELIMINATION OF MANGANESE, CARBON AND SILICATES, AND SLAG VISCOSITY ON HEAT No. 3 (57039).

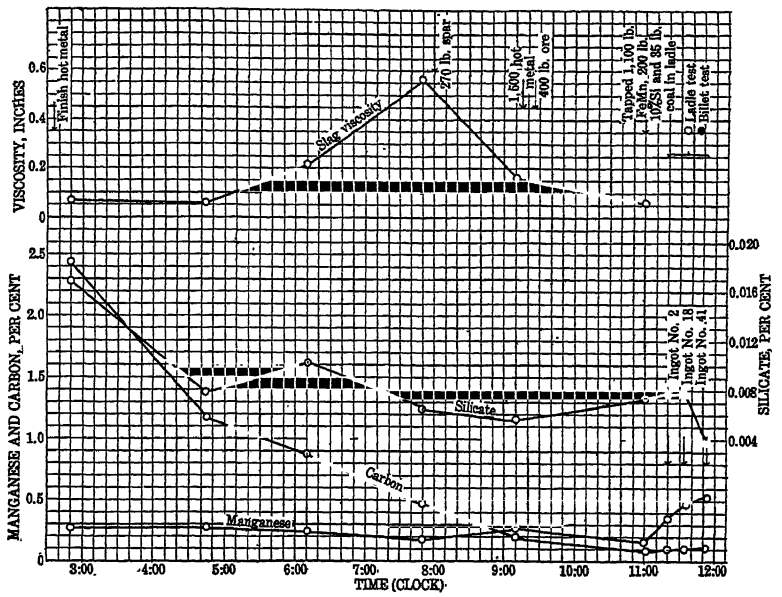


FIG. 7.—ELIMINATION OF MANGANESE, CARBON AND SILICATES, AND SLAG VISCOSITY ON HEAT No. 4 (47042).

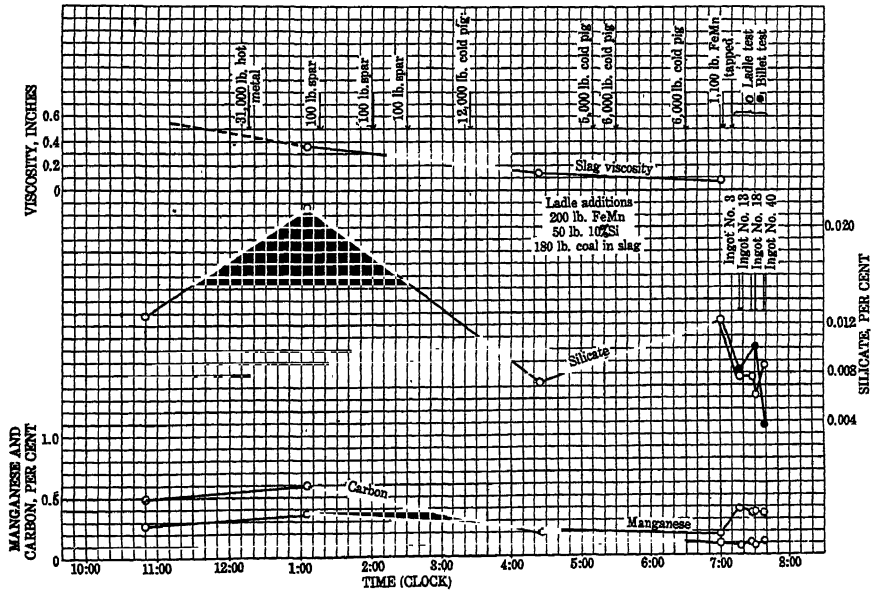


FIG. 8.—ELIMINATION OF MANGANESE, CARBON AND SILICATES, AND SLAG VISCOSITY ON HEAT No. 5 (57042).

TABLE 3.—*Comparative Details on Open-hearth Heats*

1	2	3	4	5	6	7	8	9	10	11	12
Heat No.	Scrap	Scrap, Per Cent.	Average Si in Hot Metal, Per Cent.	Carbon at Meltdown, Per Cent.	Iron Oxides in Final Slag, Per Cent.	Furnace Addition, Lb.	Ladle Addition, Lb.	Action in Ladle	Average Silicates in Hot Metal, Per Cent.	Average Silicates in Billets, Per Cent.	Average FeO in Billets, Per Cent.
1	Miscellaneous; pit scrap; punchings	49.8	0.79	0.40	Fe_2O_3 8.50 FeO 13.50	2,500 of ore	200 of 10 per cent. Si; 1100 of FeMn	Reaction on 31st ingot	0.0261	0.0075	0.058
2	Pit scrap; punchings; bundled tin	50.7	0.74	0.30	Fe_2O_3 9.50 FeO 17.45	2,000 of ore; 7,000 of cold pig	1,000 of FeMn	Quiet throughout	0.0230	0.0083	0.061
3	Crop ends	45.9	0.78	0.80	Fe_2O_3 7.95 FeO 14.65	7,500 of ore	1,000 of FeMn	Reaction on 31st ingot	0.0386	0.0097	0.056
4	Miscellaneous; bundled tin	41.5	0.43	Soft	Fe_2O_3 9.05 FeO 17.45	13,900 of hot metal; 400 of ore	200 of 10 per cent. Si; 1,100 of FeMn; 35 of coal in slag	Quiet after coal addition	0.0237	0.0063	0.040
5	Crop ends	42.5	0.22	Very soft	Fe_2O_3 10.05 FeO 18.45	29,000 of cold pig; 1,100 of FeMn	200 of FeMn; 50 of 10 per cent. Si; 180 of coal in slag	Light reaction on 11th ingot	0.0350	0.0073	0.039

No attempt was made to standardize on an identical practice for the five heats, except to produce a similar product. Closer control was not feasible, primarily because the variation in the pig iron necessitated variation in the working of the heats.

Figs. 4 to 8 show the elimination of carbon, manganese and silicates, and the condition of the slag, as indicated by its relative viscosity, on the five heats.

By way of explanation, the viscosity is measured by allowing a spoonful of slag to flow down a steel plate inclined at 30° to the horizontal. A viscous slag flows slowly and freezes in a thick layer on this plane; a thin slag gives a thin layer. The relative viscosity is then determined by measuring the thickness on the plane to the nearest hundredth of an inch, and is so shown on the plots of the five heats.

Table 3 lists the essential points of comparison between the heats; Table 4 shows the carbon content of the metal and iron oxides in the slags during the course of the heats.

TABLE 4.—*Carbon in Metal and Iron Oxides in Slags*

Heat No.	Time	C, Per Cent.	FeO, Per Cent.	Fe_2O_3, Per Cent.
1	4:09	1.60	15.31	10.60
	8:10	0.58	7.02	4.66
	9:40	0.48	7.68	1.80
	11:35	0.40	9.25	7.86
	12:10	0.27	15.05	3.84
	1:17	0.08	13.50	8.50
2	9:25	2.28	17.80	4.38
	11:00	1.46	14.72	1.37
	12:05	0.88	12.72	1.40
	12:40	0.55	12.97	7.60
	1:12	0.37	13.22	4.65
	2:12	0.07	16.00	9.25
	3:07		17.45	9.50
3	12:45	1.66	7.18	2.16
	2:20	1.08	5.98	0.98
	4:00	0.89	6.67	7.95
	4:45	0.58	15.40	5.95
	6:28	0.10	14.65	7.95
4	2:50	2.43	18.63	9.15
	4:45	1.17	14.30	2.72
	6:10	0.89	15.62	2.78
	7:50	0.47	14.05	5.00
	9:10	0.20	12.05	9.15
	11:02	0.09	17.45	9.05
5	10:50	0.49	15.58	2.00
	1:05	0.60	15.38	2.38
	4:27	0.20	15.75	7.02
	7:00	0.10	18.45	10.05

Elimination of Silicates in the Open Hearth

Table 5 shows the silicate content of the charge and the silicates in the tapping tests and billets on the five heats. The average silicate content of the charge was calculated by assuming that the general run of scrap contains 0.010 per cent. silicates and crop ends 0.015 per cent., due to segregation in ingots.

TABLE 5.—*Elimination of Silicates in the Open Hearth*

Heat No.	Average Silicates in the Charge, Per Cent.	Silicates, in Tapping Test, Per Cent.	Reduction Charge to Tap, Per Cent.	Average Silicates in Billets, Per Cent.	Reduction Tap to Ingot, Per Cent.
1	0.0181	0.0130	28	0.0075	42
2	0.0164	0.0095	42	0.0083	13
3	0.0278	0.0115	59	0.0097	16
4	0.0181	0.0073	60	0.0063	14
5	0.0265	0.0120	55	0.0073	39

With the exception of heat No. 1 the silicate content of the tapping tests increases with the silicate content of the charge. There is an average reduction of 54 per cent. silicates in the last four heats to the time of tapping. Heat No. 1 showed only 28 per cent. reduction, probably explained by the heavy slag during the last hour of the heat. This stopped the elimination of silicates and not enough time was allowed after the slag had been thinned for elimination to proceed very far.

The manganese oxide formed on the addition of ferromanganese assisted in the elimination of silicates in all heats bringing them all in the range 0.0063 to 0.0097 per cent. With this small variation and low percentage no marked difference in the quality of the steel from the five heats could be expected, if differences in quality are due to variations in silicates in the metal.

Effect of Variation of Silicon in the Iron on Open-hearth Operation

Variation in silicon in the iron affects the carbon content of the heat at the melt-down, the viscosity of the slag, the iron oxide content of the slag, the slag volume, and the erosion of the furnace lining.

1. *Carbon Content at Melt Down.*—The effect of low-silicon iron is shown in Table 3, column 5. Higher silicon iron raises the carbon content at melting just as the low-silicon iron lowered it. One of the main reasons for supplying iron of uniform silicon content to the open hearth is that more regular operation is thus assured.

2. *Slag Viscosity.*—In general, low-silicon iron causes a very heavy slag during the early stages of the heat and excessive amounts of fluorspar or ore are necessary to bring about the proper fluidity during the finishing period. On the other hand, high-silicon iron causes very thin slags which

must often be thickened with burned lime. If the slag is too thin at the end of the heat, excessive oxidation of the final additions will occur with a decrease in quality of the steel. A combination of too thin a slag with too high iron oxide content is to be avoided whenever possible. It is interesting to note in heat No. 1 that after the slag had begun to "shape up," the silicates were being eliminated steadily, and when the slag thickened after the addition of ore, elimination ceased. This has been observed on other heats and one point which should be stressed is that the slag should be in good shape as long as possible if proper elimination of non-metallic matter is to be carried out.

3. *Iron Oxide Content of the Slag.*—At the time of adding the metal to a heat, considerable scrap has melted and a slag very high in iron oxides has formed. Two of the functions of silicon in the iron are partly to reduce these oxides and to furnish SiO_2 to the slag. The result of these two actions is to keep the slag fluid when the lime comes up and to prevent its becoming excessively rich in oxides of iron. If the silicon in the iron is abnormally low the resultant slag on the bath will be high in iron oxide.

4. *Slag Volume.*—The slag volume increases with increasing silicon in the iron. Each increase in slag volume in the furnace causes a slowing up of the heat time because heat transfer to the metal is decreased. Sufficient slag should be present to bring about the desired elimination of impurities, particularly phosphorus and sulfur, but excessive amounts of slag should be avoided. Low-silicon iron will give a low slag volume, but the slag is usually viscous enough so that the decrease in weight of slag is usually more than counterbalanced by its increased viscosity, and the net result is a slow heat.

5. *Erosion of Lining.*—Excessive erosion of the lining is encountered when using high-silicon iron. Conversely, low-silicon iron causes little trouble as far as erosion is concerned, but bottoms will build up considerably due to the difficulty of getting the lime up.

Ladle Reactions

In making rimming steels there is sometimes a heavy reaction in the ladle, due to excessive oxidation of the metal by the ladle slag.

The principal factors causing ladle reactions are highly oxidized tapping slags, very fluid tapping slags, and excessively hot heats. This does not mean that any one of the three will cause a ladle reaction, but each is instrumental. If the ladle reaction is severe, carbon and manganese may be lost in amounts sufficient to cause part of the heat to be rejected on chemical analysis.

The course of the action in the ladle on the five heats is shown by Fig. 9. Billets were taken from the center of three or four ingots on

each heat. The percentages of manganese and FeO in each one are plotted to show how these concentrations changed during teeming.

On heat No. 1 there was a heavy reaction lasting from the 31st to 36th ingot, accompanied by a rise in the FeO content of the steel and a drop in manganese. On heat No. 2 the manganese was low throughout; the rise in FeO is undoubtedly due to the very high content of iron oxides in the finishing slag. Heat No. 3 reacted lightly throughout, showing a gradual drop in manganese, with rather high FeO, except at first.

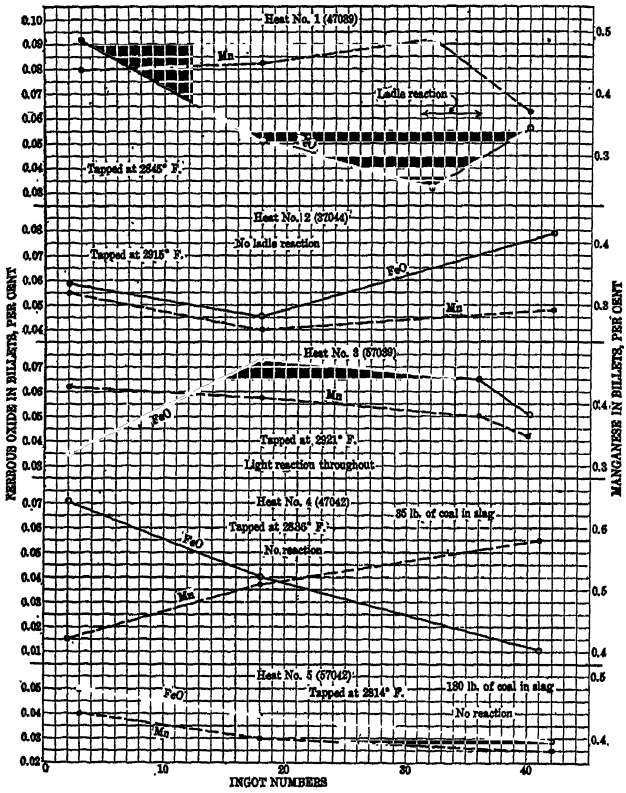


FIG. 9.—VARIATION OF FeO AND Mn DURING POURING.

On heats No. 4 and 5 a change in practice suggested by one of the writers was instituted. This consisted in throwing a small amount of coal into the ladle slag. As the reaction

$$C + FeO \rightleftarrows CO + Fe$$

absorbs heat, the action of coal on the iron oxides in the slag will result in a cooling of the latter. This should tend to cut down the violence of the ladle reaction and prevent loss of alloy additions. On heat No. 4 it will be seen that the FeO is dropping and the manganese is rising steadily during the teeming. On the last heat there is also a steady drop

in FeO, accompanied by a drop of a few points of manganese. There can be no doubt that these two heats would have reacted violently in the ladle had it not been for the chilling action of the coal in the slag. It is significant that these last two heats had a lower average FeO content in the billets than any of the first three, despite the high iron oxide in the finishing slag. No "kick-back" of phosphorus took place, indicating that the action is not excessively deoxidizing in character but merely an arresting of the interaction between slag and metal.

Effect of Silicates on Finished Steel

It is unfortunate that in none of the test heats was the steel sufficiently dirty to show defects which could be traced to silicates from the pig iron. Inspection of the extracted silicates from the steel samples shows a number of particles identical in appearance to those found in the pig iron persisting all through the heat and into the finished product. It is definitely known[3] that silicate inclusions rich in SiO_2 tend to cause red-shortness if present above certain limiting concentrations. This limit varies with the type of rolling or forging operation which the steel undergoes. Relatively smaller amounts of silicate may cause surface defects.

Table 1 shows that the quantity of silicate in the pig iron did not vary much from heat to heat; consequently, one would not expect much variation in the steel. The major irregularity in the blast-furnace operation, that which produced the highest silicate content in the pig, came at cast No. 2141. This metal occurred after the five test heats had been made, so that its effect on the steel is not known.

Conclusion

The data collected during this test are not sufficient to correlate bad iron with trouble in the finished steel. However, there are four points which indicate strongly that certain results recorded may be the main factors in the bad iron situation:

1. The open-hearth operator is of the opinion that any trouble which may be blamed on the pig iron usually comes at a time when the blast furnace is operating irregularly.

2. It is a matter of general opinion and some experimental fact that silicates in the finished steel will cause various kinds of trouble.

3. It is an experimentally determined fact that the higher the silicates in the iron the higher the silicates in the steel.

4. This test shows that the silicates in the iron are higher when the blast furnace is operating irregularly than when it is running steadily.

[3] C. H. Herty, Jr., and G. R. Fitterer: Ferrous Silicates in Steel. Atlantic City, N. J., meeting of Amer. Soc. for Test. Materials, June, 1928. See Carnegie Inst. of Tech. *Bull.* 36 (1928).

From these four points the conclusion may be drawn that if the blast-furnace operation is irregular, trouble is liable to be encountered in the finished steel. Just how irregular the operation must be before such trouble is encountered will probably vary for each blast furnace and for the different grades of steel made.

In any event the obvious remedy, as far as keeping the silicate content of the iron low is concerned, is to keep the blast furnace operating at a steady rate and at a steady chemical analysis, which is an indication of smooth operation. This means that the burden, hearth temperature, and rate of blowing should be as nearly constant as possible. Fig. 3 should not be interpreted as an infallible guide because it applies probably only to the particular furnace under investigation. It seems highly possible that a furnace with slightly differing physical and mechanical characteristics would show, for a given change in silicon, either a greater or smaller amount of silicates in the product. It is impossible to place a definite limit on the silicate content of the iron—this will depend upon particular conditions at the steel plant. Therefore the permissible variation in silicon in the pig iron above which the iron becomes dirty had best be determined by observation at the furnace in question.

If such iron is produced, however, it would be advisable to do one of two things: (*a*) give it as much time as possible in the mixer to allow particles of silica to rise from the metal to the slag; or (*b*) send the questionable casts to the pig machine, and use the pigs in small doses at the open hearth.

It frequently happens that low-silicon, high-silicate pig will be poured into the open hearth before the melter knows its analysis. In this case great care should be taken to keep the slag fluid throughout the heat. The reason for this is that such a slag more readily absorbs silica particles than a thicker one. Some of the evils attendant upon low-silicon metal may be overcome by the addition of silicon pig in suitable quantity with the hot metal, or shortly after its addition. This practice will tend to produce thinner slags as well as cut down the oxidation of the slag and make up the deficiency of heat energy associated with the silicon in normal pig iron.

Acknowledgments

The writers take this opportunity of expressing their appreciation of the cooperation of the Bourne-Fuller Co. in the test, in particular to N. K. Hartford, general superintendent, H. J. Allen, superintendent of the blast furnace department, and R. L. Cain, superintendent of the open hearth department. They also wish to acknowledge the cooperation of the Weirton Steel Co. for rolling and zinc-coating the sheets made from the five heats.

Basic Open-hearth Yields

By C. D. King,* New York, N. Y.

(New York Meeting, February, 1929)

The advances in basic open-hearth practice which have occurred during the past decade have been principally in the direction of the physical development of larger units, decreased fuel consumption and increased length of furnace campaigns. However gratifying the economies which have resulted from these improvements are, it must be granted that like advances in chemical, physical-chemical and metallurgical knowledge pertaining to open-hearth practice would have added greatly to these already attained reductions in costs and it is the purpose of this paper to stimulate the discussion and study of these phases of cooperation and their relation to ingot yields.

Definition and Calculation of Losses

In discussing basic open-hearth yields, the writer refers to the ingot yields obtained in the process of converting pig iron, scrap and ore to steel. In this conversion some scrap is produced. The difference between the total weight of ingots and scrap produced and the original metallic charge constitutes the loss. Basic open-hearth yields vary considerably, and while some of the divergencies can be explained metallurgically because of differences in slag analysis, proportion of pig charges, and character of steel made, there often remain differences that apparently do not readily disclose themselves. In reconciling yields by the usual accepted methods of calculation, one is often forced to evaluate large losses as "unaccounted for." Such a system is prone to accept these large losses as inherent to the operation and not susceptible of appraisement and correction. It is obvious that if the ingot yield plus the scrap recovered subtracted from 100 per cent. determines the loss, a drop in yield may increase the loss or the scrap, and both contribute to a monetary loss. To be sure, one can subdivide these unaccounted for losses into various components, such as metallics in slag, free Fe in slag, spillage, etc., and thereby reduce the amount of losses considered as "unaccounted for." If empirical methods could indicate with some degree of accuracy all losses, however slight, the undetermined losses become appreciably smaller and resultant calculations will check actual

* U. S. Steel Corporation.

operations with reasonable accuracy. A method of yield calculation which would disclose departures from normal good practice is therefore welcome to the open-hearth operator in affording him a rapid and accurate check on yields to be obtained for different conditions. While the method proposed is of particular value in checking average conditions over extended periods, it has, to some extent, equal value for individual heats, provided no unusual variation has obtained, such as inaccuracy of weighing, bad bottom condition, overcharging, running stoppers, etc.

Influence of Estimations

As normally considered, the Gross Metallic Charge is made up of pig iron, hot or cold, iron scrap, steel scrap, iron in ore, scale, etc., and additions. In the sense in which additions are treated in the discussion, they are the pure metallic manganese, silicon, vanadium, etc., of the ferro-alloys used, the iron content being deducted and shown under pig iron. Deducting from gross metallic mixture, all the scrap recovered such as iron scrap, pit scrap, skulls, ingot butts, condemned ingots, and where open-hearth slag is used in blast furnaces, the metallic contents thereof, one arrives at the Net Metallic Mixture.

It is assumed that in any well-managed open-hearth plant, the gross metallic mixture is weighed with a reasonable degree of accuracy, that all the scrap practical to recover is accounted for and duly credited, and that the ingots are accurately weighed. Estimated weights for any major portion of the metallic charge must result in fictitious yields for individual heats, some abnormally high and others equally low. Such practices result in large adjustments at intervals in order to balance materials on hand, and as a result the yield reported is seriously disturbed. While even with the most careful weighing, minor adjustments are necessary at times, such realignment should be small and will not disturb reported yields if all materials are weighed with a reasonable degree of accuracy. For example, if a plant using hot metal does not weigh it going to open-hearth furnaces, in addition to the irregular practice resulting from frequent repigging or excessive oreing, a large adjustment may be found necessary at the end of the month. In the operation of a plant consuming 30,000 tons hot metal monthly, an adjustment of 200 tons weekly may not be unusual. Under such conditions, regular yields cannot obtain and a check against such conditions is largely futile.

It is equally important to weigh ingots accurately if the yield reported is to be regarded without question. If the ingot weight is estimated by the method of adding rolling-mill product, scrap, scale, and a fixed heating loss to give ingot weight, it will introduce an error on the ingot weight which will vary directly with the accuracy of the empirical determination of heating losses, and the exactness of the weights for product, scale and

scrap. It would appear equally as accurate to determine hot metal received by the open hearth from blast furnaces by a similar procedure.

By the same token estimates of mill scrap charged to open-hearth departments are prone to inflate the gross metallic mixture and result in an ingot yield lower than actually obtains. Such estimates are all sources of possible error, making the check of yields at open-hearth departments difficult and of questionable value. For these reasons, the following method of determining basic open-hearth yields assumes that reasonable care is used in the weighing of all materials entering the furnace, and that all the scrap and ingots are similarly accounted for. The discussion which follows is largely based on American basic open-hearth practice.

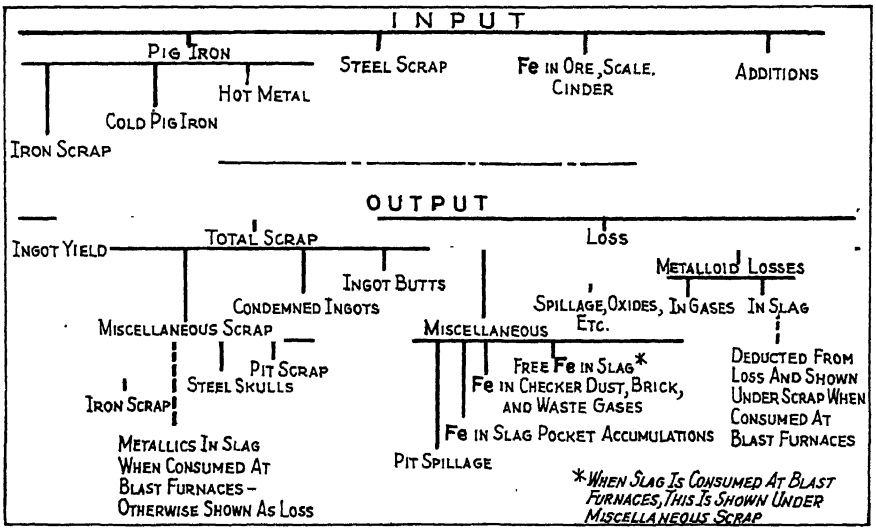


FIG. 1.—FLOW SHEET SHOWING INPUT AND OUTPUT METALLIC CHARGE IN BASIC OPEN HEARTH.

Losses in Basic Open-hearth Practice

The losses in basic open-hearth practice are usually as follows: carbon eliminated with waste gases; metalloid eliminations in slag; free Fe in slag; unrecoverable spillage; metallics lost and lodged in checker chamber dust, brickwork, and slag pockets, and carried away by waste gases; and wastage incidental to recovery and preparation of miscellaneous scrap. If the condemned ingots and ingot butts are added to this group and provision made for loss on "additions," this grand total subtracted from the gross metallic mixture gives the Ingot Yield. To facilitate the following method of calculating yields, these are grouped as Metalloid Losses; Iron Lost in Slag; Spillage; Oxidation and Losses due to Foreign Materials; and Miscellaneous Losses. Spillage refers to losses involved in handling hot metal, small irrecoverable splashings or shot, often swept up with

debris around the furnace and thus lost, while losses due to foreign materials refer to the dirt, oxides, paint, oil, moisture and other foreign materials adhering to scrap, and accounting for some difference between actual metallic weight of scrap and its normally accepted weight, even though recognition is made of its relative value for fixing prices therefor. When pig iron is used from sand-cast beds, this element must also be considered. The miscellaneous losses are made up of free Fe in slag; iron in slag pocket accumulations and checker chamber dust, waste gases, etc.; unrecoverable spillage on pit side; and losses due to extraneous SiO_2 due to erosion of furnace structure. With the relative amounts of these various losses determined, a yield calculation can be made for any charge or type of steel which will check actual good practice with satisfactory accuracy. In addition to these losses, certain scrap is produced, making it necessary to establish a standard for good practice for these elements which can be based on the experience of a plant or plants considered representative in this respect. One must also consider the loss of chemically combined iron in the slag. Fig. 1 shows a flow chart of the metallic charge and the components of the output. A simple method of yield calculation is proposed, as follows.

Method of Yield Calculation

An average analysis of final slag should be available, and where plants operate with run-off slags, the approximate proportion of run-off should be known, which combined with final slag, is readily calculated to composite slag. All slags contain SiO_2 and Fe, the latter the calculated amount from iron oxides in the slag. Free iron in the form of shot in slag is not considered, since this would be shown under miscellaneous losses as previously explained. The ratio of Fe to SiO_2 in the slag, or for convenience Si (equivalent), affords one a method of measuring the amount of iron loss in slag. It is obvious that all silicon, as metalloids eliminated, will find its way as SiO_2 in slag, that the SiO_2 content of fluxes, ores, dolomite, and some of the furnace erosion eventually appear in slag, and added to this such dirt as may accompany the charge will also be present. Therefore, knowing the amounts of SiO_2 or Si of all materials, and the amounts contributed by each, and the Fe and SiO_2 or Si content of the slag, the total Fe loss in slag can readily be calculated. The following example deals with a composite of run-off and tap slags. The same treatment obtains for plants with final slags only. In a slag (composite) showing 17.39 per cent. SiO_2 and 14.97 per cent. Fe (chemically combined), the ratio of Fe to Si is 1.85, or in other words, every part of the charge introducing 1 lb. Si carries with it 1.85 lb. Fe into slag. This necessarily requires a fairly accurate check for SiO_2 or Si, since if the total known SiO_2 or Si does not check with the amount shown in the slag, it

will result in a lower iron loss than actually obtains. It is of considerable importance to check all sources for SiO_2 or Si, since one perceives they contribute to large losses of iron in slag, proportionate to the amounts they introduce. In actual practice the ratio of Fe to Si varies considerably with the analysis of materials, the amounts of ore, limestone and pig, and type of steels made, and therefore no empirical figure can be used. It is necessary to determine this for each condition or type of steel made.

In order to clearly indicate the application of this method of calculating yields, an example is furnished. It is necessary to know a minimum of data for fairly exact calculation, *viz.:* Analysis of iron, metalloids in scrap, Fe and SiO_2 content of ore, SiO_2 content of dolomite, limestone and spar, residual in bath, average analysis of run-off and tap, or tap slag only if the former does not obtain, and the proportions of gross metallic mixture components and fluxes used in the charge. For convenience sake the analysis of materials is arranged as follows. The data upon which the illustrative calculations are based are derived from operation of a basic open-hearth plant which produces low and medium carbon steels (0.10 C to 0.50 per cent. C) and pertains to a year's production of such steels. The average slag analyses are presented in Table 1, being in the ratio of 25 per cent. run-off and 75 per cent. tap slag.

TABLE 1.—*Average Slag Analyses*

	25 Per Cent. Run-off Slag	75 Per Cent. Tapping Slag	100 Per Cent. Composite Slag
SiO_2, per cent	20.94	16.20	17.39
P_2O_5, per cent	2.25	1.85	1.95
CaO, per cent	18.90	43.99	37.73
MgO, per cent	6.93	8.26	7.93
Fe, per cent	21.96	12.64	14.97
Mn, per cent	14.48	8.14	9.73
$Al_2O_3 + TiO_2$, per cent	3.24	2.71	2.85
S, per cent	0.12	0.17	0.16

TABLE 2.—*Analysis of Materials Used*

	SiO_2, Per Cent.	Fe, Per Cent.	Si, Per Cent.	C, Per Cent.	Mn, Per Cent.	P, Per Cent.
Pig iron			1.12	4.28	1.60	0.200
Steel scrap				0.18	0.45	0.015
Ore (natural)	6.69	54.1	3.12			
Limestone	.85		.39			
Dolomite	1.69		.79			
Fluorspar	4.90		2.28			
Slag (composite)	17.39	14.97	8.11			
Residual in bath				0.12	0.16	0.015

Slag ratio, Fe to Si, 1.85.

Table 2 shows the analyses of the different charge components and it should be noted that in this table silica is converted to a silicon equivalent, *i. e.*, SiO_2 converted to Si is calculated from the atomic weight as follows: Si(28) + O_2(32) = 60 and the ratio of Si to SiO_2 is $^{28}/_{60}$ or 46.67 per cent. The Fe to Si ratio in slags is derived from the composite slag.

Table 3 shows the losses by groups of the charge components and as will be seen from Table 4, the total loss in each of the six groups shown in Table 3, multiplied by the percentage of each component charged, gives the loss per ton of total metallic charge.

TABLE 3.—*Losses in Components of Basic Open-hearth Charge*

Type Losses		Fe in Ore, Scale, Etc.	Hot Metal or Pig Iron	Steel Scrap	Lime-stone	Dolo-mite	Spar
Metalloid losses	Carbon, per cent		4.16	0.06			
	Silicon, per cent		1.12				
	Manganese, per cent		1.44	0.29			
	Phosphorus, per cent		0.185				
Iron loss in slag (Fe to Si ratio), per cent		10.67	2.072	0.09	0.74	1.46	4.24
Spillage, oxides, foreign losses, per cent			0.50	0.40			
Miscellaneous losses, per cent		0.75	0.75	0.75			
Total losses, per cent		11.42	10.227	1.59	0.74	1.46	4.24

It will be noted that the components are arranged to show the Si equivalent of materials carrying SiO_2 into the slag. The losses of the various parts of the charge can be conveniently arranged in groups showing Metalloid Losses, Iron Loss in Slag (Fe to Si ratio), Spillage, etc., and Miscellaneous Losses. One then arrives at the total loss involved in each part of the charge.

The metalloid losses are the difference between those contained in the pig iron and scrap and the residual in the bath. The iron loss is merely the product of the Si shown for each component times the Fe to Si ratio in the slag, which in this instance is 1.85. In the case of ore, since this is shown on the natural basis in Table 2, and must be converted to iron base for Table 4, the calculation is as follows: $\frac{3.12}{54.1} \times 1.85 = 10.67$. It will be observed that these total losses do not mean that each metallic constituent actually loses by weight such percentages, but by such an arrangement, an easy method is possible in determining losses. The item of spillage as applied to pig iron will be explained in detail as will oxides and foreign materials and miscellaneous losses. Suffice it to say, for ease in following the method, that spillage on hot metal refers to losses involved in handling from mixer to open-hearth furnaces as well as mixer

losses, that oxides and foreign materials apply to steel scrap, and to cold pig iron when sand-cast, and that miscellaneous losses involve losses in slag pockets, checker dust, unrecoverable spillage on pit side, free Fe in slag, and SiO_2 from furnace structure. Where cold iron is used the same method applies except no allowance is made for spillage. The loss of 0.09 per cent. shown on steel scrap is due to SiO_2 contained as dirt in scrap. Having obtained the total losses on each component in the charge, it is only necessary to multiply such by the percentages of these materials in respect to total metallic charge. It should be stated, and will be later amplified, that the loss on additions represents the loss obtained on the pure alloys since the iron content for convenience sake is normally shown under Pig Iron. The results obtained are presented in Table 4.

TABLE 4.—*Calculation of Basic Open-hearth Yields*

Materials	Materials Used per Ton Metallic Charge, Per Cent.	Losses in Charge Components, Per Cent.	Loss per Ton of Total Metallic Charge, Per Cent.
Fe in ore, scale, etc.	5.4	11.42	0.617
Hot metal	56.3	10.227	5.758
Steel scrap	37.8	1.59	0.601
Additions	0.5	25.00	0.125
Total metallic charge	100.0		7.101
Limestone	6.9	0.74	0.051
Dolomite	2.7	1.46	0.039
Fluorspar	0.35	4.24	0.015
Total losses			7.206
Metallics recovered in slag			
Net losses			7.21
Scrap recovered:			
Miscellaneous scrap			3.80
Condemned ingots and ingot butts			1.00
Metallics in slag			
Total scrap			4.80
Total net loss and scrap			12.01
Ingot yield			87.99
Total			100.00

It will be noted that the total losses on the metallic charge are 7.10 per cent. (Table 4), while dolomite, limestone and spar, because of their SiO_2 content, contribute 0.105 per cent., or a total of 7.21 per cent. The small loss caused by these fluxes is a direct result of their low SiO_2 content.

It is obvious that if the amounts used were larger and particularly were the SiO_2 contents higher, these losses can become appreciable. For convenience in calculation, all the dolomite or the SiO_2 thereof is assumed to enter slag. Since the error might be 10 to 20 per cent., the total possible error is 0.005 per cent., or negligible. Where blast furnaces consume open-hearth slag, the total losses are reduced by the amounts used and the metallic contents thereof. This recovery in some cases may be as high as 3.0 per cent. or more per ton of metallic charge, and while no difference is shown on yields, a credit is made for scrap, thereby increasing the proportion of scrap recovered and decreasing loss. In this analysis no credit is assumed. The calculated yield after allowing for the actual scrap recovered is 87.99 per cent. For the period of one year this plant showed an ingot yield of 88 per cent., which can be considered a perfect check.

It cannot be assumed that the above method will check all conditions with such accuracy, but it has been applied to innumerable varieties of conditions with satisfactory results. It will be observed that the total scrap was 4.8 per cent., made up of 3.8 per cent. miscellaneous and the balance condemned ingots and ingot butts. Could it be shown that such a recovery is not consistent with good practice, then the actual yield of 88 per cent. is low to the extent of the decrease in scrap. For example let us assume that the total scrap should have been 4 per cent., then the calculated yield would be approximately 0.80 per cent. higher, or 88.79 per cent., than that actually obtained, and since the difference lies in scrap produced, one can investigate the source of the high scrap production.

In explanation of the use of certain standards in determining losses on components of charge, and with particular regard to spillage, oxides, etc., and miscellaneous losses, the following is offered.

Miscellaneous Losses

Miscellaneous losses, as indicated in the Fe to Si ratio method for calculating ingot yields, are made up of iron lost in slag pocket accumulations, checker chamber dust and stack losses, free metallic iron in slag, loss due to SiO_2 contributed by erosion of furnace structure, and non-recoverable pit spillage.

Iron Loss in Slag Pockets

It is evident from the large amounts of material taken out of slag pockets at furnace rebuilds or other times, and from the analysis of same, that appreciable amounts of iron are lost in this manner. Determinations of the amounts of slag in pockets show wide variation with respect to type of charge used, fuel and construction of furnace. In an

investigation[1] conducted by the Bureau of Mines, some interesting figures were disclosed. One plant operating stationary basic open-hearth furnaces on producer gas, showed an accumulation of 14.33 lb. slag per ton of ingots. This was the equivalent of 6.5 lb. Fe or 0.29 per cent. per ton of ingots. On a duplex furnace, this amounted to 3 lb. slag per ton of ingots or the equivalent of 0.06 per cent. Fe per ton ingots, while another duplex furnace showed about the same amounts. The writer submits some tests at various American plants which show for a natural gas-fired stationary open-hearth furnace over a period involving 25,212 tons ingots, or 469 heats, a total of 143,000 lb. slag or approximately 5.7 lb. per ton of ingots. This material analyzed 44.72 per cent. Fe_2O_3 and 14.85 per cent. FeO. The equivalent loss of Fe was 2.44 lb. or 0.11 per cent. per ton of ingots. Two recent tests on an oil-fired open-hearth furnace show 0.16 per cent. Fe on a 60-ton furnace and 0.25 per cent. on a 45-ton furnace. On a furnace fired with by-product coke-oven gas, a total of 129,800 lb. slag were found in slag pockets during a run of 352 heats or 22,416 tons ingots. This was equal to 5.8 lb. slag per ton ingots or 2.04 lb. Fe equal to 0.091 per cent. Fe per ton ingots. A tar-fired furnace showed the equivalent of 16.35 lb. slag per ton ingots equal to 0.35 per cent. Fe lost per ton ingots, an exceptionally high amount, but typical to some degree of the large losses involved with liquid-fuel-fired furnaces. Variations are shown from 0.06 to 0.35 per cent. Fe lost per ton of ingots, and in order to establish definite standards for calculation,

TABLE 5.—*Analysis of Slag Pocket Accumulations*

	Producer Gas				Natural Gas	Tar	Coke-oven Gas	Fuel Oil	
	North Gas	South Air	South Gas	North Air					
FeO, per cent	44.72	19.63	35.07	20.78	14.85	17.34	14.81	15.40	
Fe_2O_3, per cent	12.54	33.84	18.00	33.31	44.72	48.46	33.72	37.10	
SiO_2, per cent	30.52	36.22	28.04	37.19	26.90	26.02	36.43	37.70	
P_2O_5, per cent	0.21	0.21	0.18	0.16	0.62	0.25	0.05	0.23	
MnO, per cent	2.81	1.89	3.02	1.93	1.29	1.07	0.72	1.50	
Al_2O_3, per cent	1.10	0.99	2.64	1.06	4.47	0.67	8.02	1.25	
CaO, per cent	6.86	6.36	5.88	5.02	5.32	3.39	3.02	4.50	
MgO, per cent	1.11	0.70	0.83	0.41	1.83	0.79	1.17	1.81	
Total slag per ton ingots, lb.	14.33				5.70	16.35	5.80	8.70	14.10
Fe per ton ingots, lb.	6.50				2.44	7.75	2.04	3.48	5.64
Fe per ton ingots, per cent	0.29				0.11	0.35	0.09	0.16	0.25

[1] B. M. Larsen, F. W. Schroeder, E. N. Bauer and J. W. Campbell: Service Conditions of Refractories for Open-hearth Steel Furnaces. Carnegie Inst. Tech. *Min. and Met. Investigations Bull.* 23 (1925).

it appears that no great error is introduced by allowing the equivalent of 0.20 per cent. Fe loss per ton of metallic charge in slag pocket accumulation. Some characteristic analyses of deposits in slag pockets are shown in Table 5 for different fuels.

Iron Loss in Checker Chamber Dust

In the matter of checker chamber dust, there is a like variation with different fuels. In the investigation referred to,[2] a test was made involving 16,254 tons of ingots on a duplex furnace, in which the total checker dust during this period of operation was found to be 61,765 lb., or 3.8 lb. per ton of ingots. At approximately 50 per cent. Fe content, this is the equivalent of 0.09 per cent. Fe per ton of ingots. Amplifying this further from various tests made to indicate amounts of dust deposited in checker chambers, we find that at the plant using natural gas, the amount of dust was the equivalent of 1 lb. per ton of ingots. The iron content of this dust was approximately 60 per cent., or equal to 0.025 per cent. Fe per ton of ingots. On a tar furnace, a similar determination was made over a period in which 15,782 tons of ingots were produced, which showed an accumulation of 93,800 lb. dust or 5.94 lb. per ton of ingots. The iron content was approximately 60 per cent., thus giving approximately 3.6 lb. Fe per ton of ingots or 0.16 per cent. Fe per ton of ingots. Another determination on a tar-fired furnace showed the equiva-

TABLE 6.—*Analysis of Checker Chamber Dusts*

	Producer Gas*		Natural Gas	Tar		Coke-oven Gas	Fuel Oil	
	A	*B*		1	2		Checkers	Boiler Tubes
SiO_2, per cent	7.30	10.75	1.88	3.78	1.22	2.30	4.70	
FeO, per cent	1.30	5.32		0.51				
Fe_2O_3, per cent	70.91	65.28	85.28	86.60	61.61†	52.72†	56.00†	24.50†
MnO, per cent	0.85	0.43	0.66	0.55	0.65	1.21	0.71	0.77
Al_2O_3, per cent	4.60	9.15	5.37	2.38	0.34	0.82		
CaO, per cent	7.60	3.55	3.50	3.15	1.53	3.45	4.80	
MgO, per cent	3.69	1.60	1.12	1.37	0.94	2.50	Zn, 3.4	Zn, 14.2
Total dust per ton ingots, lb	3.8		1.00	5.94	11.97	1.80		
Fe per ton ingots, lb	1.9		0.60	3.60	7.37	0.95		
Fe per ton ingots, per cent	0.085		0.026	0.16	0.33	0.042		

* *A*, air-chamber deposit on top of checker brick; *B*, gas-chamber deposit on top of checker brick.

† Represents Fe equivalent.

[2] B. M. Larsen et al.: *Op. cit.*

lent of 0.33 per cent. Fe lost per ton of ingots, an unusually high figure. A coke-gas-fired open-hearth furnace, on a run of 22,416 tons ingots showed the equivalent of 1.8 lb. dust per ton ingots, equal to 0.042 per cent. Fe. The writer calls attention to the high Zn content of checker-chamber and boiler-tube deposits at one plant using cold iron and high scrap charges. If one also allows for oxide absorption by checker brick work and that lost in waste gases, it appears that approximately 0.15 per cent. Fe per ton of metallic charge may be regarded as lost in this fashion. Therefore, for purposes of calculation the standard used is 0.15 per cent. Fe per ton of metallic charge. Since various fuels show a wide range in amounts of Fe lost in this fashion, it is apparent that for exact balances, individual plant investigations are necessary. Table 6 shows characteristic analyses of checker chamber deposits.

Free Metallic Iron in Slag

The reported analysis of the free metallic iron content of slags exhibits great variations. While some of this no doubt is occasioned by actual differences in practice, a sensible part of the divergency exists in methods of making magnetic determinations. Where the slag is not ground sufficiently fine, it is possible to show a higher Fe content (free iron) than is actually present because of the presence of considerable amounts of slag with the metallic particles and such errors can actually double the true amount of metallic iron. For this reason excessive reported percentages of free Fe in slags should be investigated and the methods employed in making magnetic determinations checked before considering the practice in the open hearth faulty. It is true, however, that high bottoms may cause excessive iron losses in this fashion on run-off slags. Table 7 shows the average Fe (free metallic iron) in slags for some American plants. Some of the variation may be attributed to methods of analysis and therefore must be accepted with reservations. In various publications we have seen reports of even higher percentages, but question whether such analyses are truly indicative of normal good practice. Some of the figures represent reported analyses of composite open-hearth slags at blast-furnace bins, prior to use in these furnaces, and for these no individual determinations are shown for the run-off, tap or ladle slags. In some plants no run-off slags obtain.

It would appear that the average free metallic Fe in slag, while varying considerably, may be assumed for purposes of calculation at a figure commensurate with good practice. For our purposes, this figure is taken at 1.5 per cent. by weight of slag and at an average of 13.5 per cent. slag volume per ton of metallic charge this is equivalent to 0.20 per cent. per ton. Since slag volumes vary considerably, say from 10 to 20 per cent. per ton metallic charge, this can create an error of 0.10 per

cent. in calculations for yield, and if investigation should show actual amounts in excess of 1.5 per cent., the error can be even greater in proportion. For this reason, one should determine the actual amounts with due care, and make such adjustment as may be found necessary to the standard of 0.20 per cent. per ton metallic charge. Where amounts are very much in excess, investigation should be made of causes for this excessive loss. The amount of free metallic iron in slag is the cause for much higher losses and lower yields than is generally appreciated. For even closer calculation than represented by the adoption of the standard used, one can add the free Fe in slag to that shown as chemically combined and readjust the Fe to Si ratio on this base. In this event, the miscellaneous losses, as herein indicated, should include no allowance for same.

TABLE 7.—*Percentage of Free Metallic Iron in Basic Open-hearth Slags*

Slag No.	Run-off	Tapping	Ladle	Composite
1	0.85	0.30	2.67	1.25
2	0.77	0.99	5.97	2.50
3	0.88	0.91	1.55	1.95
4	1.00	0.82	2.71	2.14
5				3.63
6				1.60
7				0.40
8				4.86
9	2.46	1.45	0.87	2.20
10		0.60	0.80	0.65

Iron Loss Due to Furnace Structure, Etc.

Since the existence of SiO_2 in the charge is accompanied by an iron loss in the slag, it is obvious that the erosion of some parts of the furnace structure, side walls and roof particularly, contributes to the silica content of the slag and is therefore the cause of a further loss of iron. One must empirically establish a figure for this loss. Dichmann[3] shows by actual tests that the erosion of brickwork causing increase of SiO_2 in slag amounts to 0.15 per cent. per ton of metallic charge. Kinney[4] shows the equivalent of approximately 0.10 per cent. Measurements of wall and roof erosion are difficult to obtain accurately, but various tests conducted at several plants show a range of 0.06 to 0.10 per cent. These figures represent the average over the life of the furnace, since in the early part

[3] C. Dichmann: The Basic Open-hearth Steel Process. 1911. D. Van Nostrand, New York.

[4] C. L. Kinney, Jr.: Economic Significance of Metalloids in Basic Pig Iron in Basic Open-hearth Practice. *Trans.*, A. I. M. E. (1924) **70**, 136.

of the furnace run, this ratio may be considerably higher. If the average slags show a ratio of Fe to Si of 1.85, which is typical of most slags making medium-carbon steels, the loss of iron is $0.10 \times 46.67 \times 1.85$ = approximately 0.086, called 0.09 per cent. per ton of metallic charge. The losses involved in handling steel from ladle pit to molds are difficult to determine, but it is obvious from a glance at pit sides of open-hearth plants, that they are not inconsiderable. These are due to spittings, splashings on way to molds, and at molds. Any assumption of the amount involved is subject to error, but for purposes of this calculation is established at 0.11 per cent., because such a figure has furnished a check on carefully conducted tests for yields.

While a loss of 0.15 per cent. is shown for Fe lost in checker chamber dust, brickwork and waste gases, and 0.11 per cent. for unrecoverable pit spillage, more thorough investigation may determine that the former losses are even higher and the latter proportionally lower. More definite information on volume of waste gases and iron losses therein are needed to establish greater accuracy on this standard.

The various Fe losses per ton of metallic charge comprising miscellaneous losses are made up as follows:

	Per Cent.
As slag in slag pockets	0.20
As dust in checker chambers, waste gases, etc	0.15
As free metallic Fe in slags	0.20
Due to erosion of furnace structure	0.09
Due to unrecoverable spillage—pit side	0.11
Total	0.75

From these empirical determinations, one can assume that every unit of the metallic charge suffers a loss of 0.75 per cent. in the form of these miscellaneous losses. Obviously differences should be allowed when comparing coke gas, natural gas, and liquid-fuel-fired furnaces.

Spillage, Oxides and Foreign Losses

In all reports on basic open-hearth yields, one is forced to assume that the hot metal designated as consumed by the furnace, represents all that is actually received. That this is far from true will be recognized when it is considered that at many plants no provision is made for a deduction of the kish or blast-furnace slag that may accompany the hot metal from blast furnaces to mixer. If the kish has been deducted from the gross metal, even if estimated on the basis of occasional checks, then for practical purposes, the reported net weight is sufficiently accurate. However, failure to account for kish, etc., is productive of possible serious errors in yield, particularly so on high hot metal charges. This will be better understood from the analysis of kish and the weights thereof per

ton of metal. The analyses, to be sure, vary considerably, largely due to the accuracy or care with which this skimming is done.

To skim kish from blast-furnace transfer ladles as the metal is poured into the mixer is difficult and often unsatisfactory, especially so since appreciable amounts of iron may be retained in the ladle and produce a poor class scrap if thoroughness in skimming is desired. Where skimming is practiced on a less thorough scale, the amount of kish thus retained in the ladle may be negligible. However, if plants find it more convenient to make no such separation and permit entry into the mixer, by slow and careful pouring into the spout at the open-hearth furnace the kish and slag can be retained in the transfer ladle and subsequently taken into account. From the standpoint of yield determination, it makes no difference which practice is followed, if the amount of such foreign material has been accounted for and deducted from gross metal. Unless this is done, the yield indicated will show lower than should actually obtain. The high silica and sulfur contents make it advisable that none of this material enter the furnace. Some kish analyses are shown in Table 8. Qualifications must be made, since the analysis will vary with the degree of separation obtained.

TABLE 8.—*Analysis and Percentage of Kish per Ton Hot Metal*

	No. 1	No. 2	No. 3	No. 4	No. 5		"Graphite" Kish	
					Magnetic	Non-magnetic		
SiO_2, per cent....	25.90	7.80	35.65	15.56	6.14	38.17	2.97	8.37
Fe, per cent.....	19.86	22.10	6.40	21.22	84.24	12.48	6.28	21.06
Mn, per cent.....	1.95	2.92		1.59	2.52	3.88		0.73
Al_2O_3, per cent...	10.07		9.52	4.21	1.25	9.50	0.94	4.91
CaO, per cent....	12.07	4.08	25.86	1.81	2.40	20.00	0.72	1.25
MgO, per cent...	2.60	0.57	2.07		0.23	1.56		0.40
Carbon, per cent.	26.30	49.36	15.27	45.58		10.77	86.46	61.63
Sulfur, per cent..	1.26	0.32	0.79					
Amount per ton hot metal, per cent.....	0.90		1.20	2.86	2.70			

If it is the practice to assume a representative fixed credit for kish, iron contents be what they may and same is deducted from gross hot metal, then no yield inaccuracies result from this source. However, if as indicated, at least 1 per cent. kish is part of the gross metal and no consideration is given it, then on a 50 per cent. hot metal charge, the yield will show an error of at least 0.50 per cent. The yield in such cases will be fictitiously lower, and the cause for many apparent low yields may be found in this condition. If the kish is in greater amounts than

1 per cent., the yield will show a larger decrease, amounting to as much as 1 per cent. on high hot metal charges. Because of the marked influence of this factor on open-hearth yields, one must be certain as to the manner in which kish is handled at any plant, and where not deducted from gross hot metal, allowances must be made therefor on calculated yields. In all comparisons of yields which are discussed here, it is assumed that such deductions have been made, and that the metal charged to open-hearth furnaces represents the net hot metal.

Iron Scrap

In transferring hot metal from the mixer to open-hearth furnaces some scrap is produced at the mixer spout, as skulls in transfer ladles, and when pouring into furnaces. By far the largest part is produced as skulls, and the amounts involved will vary at different plants, ranging as a rule from 0.20 to 1.00 per cent. per ton of hot metal, the averag being approximately 0.50 per cent. Unless it is practice to light-weigh ladles, an error in yield will obtain proportionate to the amount of such iron scrap produced. Such scrap is recovered and later prepared for either blast-furnace or open-hearth use. It therefore does not constitute an actual part of the charge which is normally shown against the furnace. For great accuracy, one should not consider any elimination of metalloids on this portion of the hot metal. However, the error involved is small when such scrap amounts to 0.50 per cent. or less. For example, if the hot metal charge is approximately 50 per cent., the error in yield is 0.025 per cent., and this would tend to give a yield higher than the calculation would show. Therefore, no provision is made for this factor in normal calculation, but where this scrap is of greater magnitude and particularly on high metal charges of 50 per cent. and over, it should be considered in the calculation. Moreover, where this obtains, the high scrap production should be investigated.

Spillage and Other Losses

In handling hot metal at mixer to open-hearth furnaces, mechanical losses in the form of shot, spittings and splashings, occur which can only be accounted for by "difference"—total metal (hot) received less that charged to open-hearth furnaces—the difference being made up of scrap and losses. These losses, together with those which occur in the mixer, normally amount to 0.50 per cent. per ton of hot metal and, therefore, in the consideration of losses on hot metal, this factor is applied. While such losses would be slightly lower for plants which can charge the desired hot metal in one ladle than for those which require more than one ladle, for practical purposes, 0.50 per cent. is used as a standard in all cases. An exception is made only in the case of plants using large pro-

portions of blown metal as in basic duplex operations, which may require four or more ladles of such metal, in which case 0.80 per cent. for spillage is allowed.

Foreign and Oxidation Losses in Steel Scrap

It will be observed that an allowance of 0.40 per cent. has been made for losses on steel scrap due to oxidation of such scrap prior to charging, scale, dirt, oil, paint or other foreign materials. At best this can be considered only an estimate. However, this figure has served to give closer checks on carefully conducted tests. Naturally, an adjustment should be made, depending on type of scrap used. On clean, heavy scrap, this might be extremely small, whereas on highly oxidized scrap it may be a considerable factor.

While actual losses in the form of iron oxidation in open-hearth furnaces are difficult to determine in so far as they pertain to the yield, it is interesting to note some recent work done by Herty[5] which discloses a high FeO content for light scrap as compared to heavy scrap in melting down. This does not necessarily mean greater iron losses *per se*, but since it involves a larger pig iron charge for the light scrap to obtain the same melt, the metalloid losses per unit of metallic charge are higher and, therefore, the yield is lower.

Heat	Type of Scrap	FeO Formed per 100 Lb. Scrap, Lb.	Time from Charging Scrap to Hot Metal Addition
A	Large	1.76	2 hours 56 minutes
B	Medium	8.35	2 hours 50 minutes
C	Medium	8.33	3 hours 13 minutes

Some interesting work was reported by Bulle,[6] showing the influence of different scrap and pig iron conditions on the operation of the open-hearth furnace. While the influence of various scrap on yields is clouded by the use of greater pig iron proportions for heavily oxidized and light scrap, therefore giving lower yields, it is interesting to note his observations on loss in scrap in open-hearth operation: "First, the evaporation or melting away of the coverings, as lead, zinc, tin, enamel, lac, ammonium chloride, etc., at Works C, 0.42 per cent. of charge. Second, the melting away of sand and slag clinging to own scrap, at Works C, 0.40 per cent. Third, the driving out of the oxygen and hydrogen content in the rust of the scrap, at Works C, 3.2 per cent. of the charge." These figures are considerably higher than those used as our standard for calculation

[5] C. H. Herty, Jr.: Basic Open Hearth Practice. *Trans.* Am. Soc. Steel Treat. (Sept., 1926).

[6] G. Bulle: Report No. 137, Steel Works Committee, Verein Deutsche Eisenhuttenleute. *Stahl u. Eisen* (1928) **48**, 320.

and the difference can be accounted for by the unusually poor type of scrap used.

Some further investigation along these lines by Lowry[7] shows scale amounting to approximately 0.10 per cent. of the weight of the scrap at the open hearth, in an analysis of two carloads of annealing pots. This same shipment when being prepared for consumption at the shipper's yards, showed a loss of 16.1 per cent. in the form of scale.

Except in rare instances where a plant is specially favored, an examination of the aggregate steel scrap making up a furnace charge such as light scrap, oxidized scrap, own mill scrap, borings, turnings, and many forms of purchased scrap, shows that there is a visible amount of dirt, oxides, paint, oil, moisture, etc. Analysis of checker brick deposits discloses at times surprising amounts of zinc. All these constitute a definite loss in the furnace. The difference between the actual metallic and the usual accepted weight will give some measure of this loss, apart from that occasioned by the introduction of silica in the charge and the resultant increase in slag volume and iron loss. While pit scrap is charged at a net weight, one wonders how accurately such a factor actually represents the true metallic weight of this type of scrap. Determinations of the amounts of such foreign materials would be of considerable help in any yield investigation and while difficult would no doubt repay such efforts. For this calculation, such losses in steel scrap, due to the causes mentioned, are set at 0.40 per cent. per ton steel scrap.

Loss of Iron Due to SiO_2 and Si in Steel Scrap

In the previous calculation shown as "Losses in Components of the Charge," a loss of 0.09 per cent. appears against steel scrap due to Fe loss in slag based on Fe to Si ratio in slag. This is due to the loss of 1.85 Fe (ratio of Fe to Si in slag) for the 0.10 per cent. SiO_2 in steel scrap. A figure of 0.10 per cent. is allowed arbitrarily, and an examination of actual conditions discloses this to be conservative. For example, if 2 per cent. of the total metallic charge is pit scrap, then on a 50 per cent. scrap charge, pit scrap constitutes 4 per cent. of the total scrap charge. If the pit scrap, even though carefully prepared at the skull cracker, contains as much as 10 per cent. slag by weight, it is equal to 0.40 per cent. slag on total scrap charge. If the slag analysis is approximately 15 per cent. SiO_2, this is equal to a total of 0.06 per cent. SiO_2 on total scrap. Larger amounts will increase this proportionally. In view of the large losses due to introduction of SiO_2, a careful preparation of pit scrap is desirable, but the extent to which this should be carried remains for investigation. In addition, dirt and sand will be found attached to

[7] E. J. Lowry: Iron in Steel Scrap. *Year Book*, Am. Iron and Steel Inst. (Oct., 1924).

many forms of light scrap and the poorer forms of market scrap. Therefore, in assuming 0.10 per cent. SiO_2, this appears within reason, especially so since many types of scrap contain silicon which in small amounts are not reported in analyses. Where silicon scrap of known analysis is charged, the Fe to Si ratio should be calculated accordingly. For the SiO_2 content assumed, and with the ratio of 1.85, the loss of Fe in slag per unit of steel scrap is $0.10 \times 46.67 \times 1.85 = 0.086$, called 0.09 per cent. The Fe loss for this factor will vary in accordance with ratio of Fe to Si in slags.

Loss of Additions

The loss of additions, which refers to pure manganese, silicon, chrome, vanadium, etc., of the ferro-alloys used, varies in actual practice depending on slag conditions, presence of other oxidizable elements, temperature, time allowed for deoxidizing action and other factors. Any standard for efficiencies must necessarily be based on normal good practice. Since manganese and silicon constitute the largest proportion of additions used, their influence is shown on the assumption of 75 per cent. efficiency or 25 per cent. loss. Where they represent a smaller part of the total alloys, adjustments are necessary on this standard. The figures in Table 9 indicate efficiencies for various alloys under a variety of conditions, the efficiencies referring to the pure metallic manganese, etc.

Table 9.—*Efficiencies of Alloys*

	Manganese, Per Cent.	Sulfur, Per Cent.	Silicon, Per Cent.	Chromium, Per Cent.	Vanadium, Per Cent.	Molybdenum, Per Cent.	Nickel, Per Cent.
Test No. 1	73.8		88.0	94.6	90.9		
Test No. 2	64.6		72.5	79.6	86.2		
Test No. 3	70.6		92.1	94.6		91.1	
Test No. 4	71.4		91.8	90.6			
Test No. 5	87.7		95.6				
Test No. 6	63.4	80.5	71.6				
Test No. 7	60.9	76.0	73.5				
Test No. 8	66.1	80.1	81.5				
	79.0[8]			65.9[9]		87.8[9]	97.0[9]
	56.0[8]			65.5[9]		86.0[9]	93.5[9]
	66.0[8]			70.1[9]			
	80.0[9]		85.0[9]				
Plant average	79.4		77.5	86.2			
Plant average	70.0		74.5	72.5			
Plant average	68.0		74.0				

[8] C. H. Herty, Jr.: *Op. cit.*

[9] A. N. Diehl: Data Relating to Basic Open Hearth Steel. Am. Iron and Steel Inst. *Year Book* (1926) 54.

Net Losses

The foregoing is an explanation of the character of the losses and the factors used in accounting for them. As previously indicated, it is necessary only to multiply these by the percentage of the material used per ton of metallic charge, after considering the analysis of the metallic and nonmetallic material going into the furnace. If the blast furnaces consume some part of the open-hearth slag, the metallics thereof are credited to the open hearth and thus regarded as a scrap credit, the percentage to be deducted from total losses being the amounts used per ton of metallic charge with due regard for the metallic contents. The latter is usually a set figure for any plant based on the average analysis of such slags. For example, if a plant produces 15 per cent. slag per ton metallic charge and the total metallics including included shot is 27 per cent., and the blast furnaces find it convenient to use about one-third of the total slag produced, there results a credit of 5 per cent. $\times$ 27 per cent. = 1.35 per cent. per ton metallic charge which should be deducted from the total losses to give net losses.

Miscellaneous Scrap

In addition to credit for scrap in the form of open-hearth slag recovered in blast furnaces, Miscellaneous Scrap, Ingot Butts and Condemned Ingots constitute part of the scrap recovery. Miscellaneous scrap includes iron scrap, pit scrap, steel skulls, mold splashings, etc. By far the largest part is contributed by pit scrap and usually amounts to 60 to 85 per cent. of the total.

Iron Scrap

Iron scrap has been treated of previously in indicating the scrap production involved in handling hot metal. This, when recovered, is credited to the open-hearth department. In normal operations, this amounts to 0.50 per cent. or less per ton of hot metal and therefore, per ton of metallic charge would be proportionate to the amount of hot metal used.

Pit Scrap

The production of pit scrap varies considerably. Table 10 shows some typical pit scrap productions per ton of metallic charge for several hot metal plants. These figures cover long periods of time. Since cold iron plants would show no credit for iron skulls, etc., miscellaneous scrap for such plants is proportionally lower. The figures represent the percentage per ton metallic charge.

TABLE 10.—*Various Types of Miscellaneous Scrap Produced per Ton of Metallic Charge*

Plant No.	Pit Scrap, Per Cent.	Iron Skulls, Per Cent.	Steel Skulls, Per Cent.	Total, Per Cent.
1	2.97	0.21	0.25	3.43
2	2.51	0.28	0.12	2.91
3	2.76	0.43	0.28	3.47
4	1.70	0.30	0.62	2.62
5	3.12	0.59	0.25	3.96
6	2.73	0.41	0.25	3.39
7	2.97	0.56	0.25	3.78

Some of the variations in the individual items are due to physical conditions, handling facilities, type of steel made, how poured, the size of ladle relative to heat and the degree to which furnaces are overloaded. For hot metal plants it appears that an aggregate of 3.0 per cent. miscellaneous scrap can be used for a standard. This would infer good practice. Where higher percentages than this figure prevail, it appears deserving of investigation. Cold iron plants should be rated lower, proportionate to difference in iron scrap produced for equal percentages of pig iron. When dealing in percentages of materials, amounts actually involved over a period of a month or a year are usually not apparent. For example, were a plant producing 0.50 per cent. higher than such a standard and based on let us say, 50,000 tons of ingots monthly, this is the equivalent of approximately 250 tons times the yield or, roughly, 225 tons. By careful drainage of furnaces and the use of ladles sufficiently large to take care of overcharged furnaces, one can increase the ingot yield by decreasing scrap production. It is interesting to note further how losses in converting pit scrap for use, may occur. To illustrate, let us assume that 1000 tons of pit scrap is sent from the open hearth to the skull cracker, which will be considered at 85 per cent. metallic content. In preparing this material, handling, etc., as much as 10 per cent. loss may occur so there is available to the open hearth approximately 900 tons at 85 per cent., or 765 tons. In other words, there is an approximate loss of 85 tons of steel or the equivalent of approximately 0.30 per cent. on the total metallic charge. This loss will naturally vary with the quantity and kind of pit scrap produced and with the care with which it is handled at the drop. For the purpose of checking yields for various practices, one is forced to assume a standard which in this case is represented as Total Miscellaneous Scrap produced per ton of Metallic Charge, equal to 3.00 per cent.

Condemned Ingots and Ingot Butts

In addition to the type of scrap already considered, there is further the production of condemned ingots and ingot butts. Condemned ingots

at most plants is largely a question of rigidity of physical and chemical specifications. It will vary considerably from plant to plant, depending largely on the type of steel made, the tolerance in specifications and the standards of inspection for quality. An average total of both items at well-conducted plants amounts usually to 1 per cent. per ton of metallic charge. Inspection of molds, careful pouring and care in producing steel to come within chemical specifications, can assist materially in keeping such scrap within the figure mentioned. Ingot butts are largely dependent on the minimum size ingot that can be rolled. The length of the ingot butt that can be handled by rolling mills determines this factor and where plants are held to one size ingot or mold, there is little chance for improvement in this type of scrap production. Where plants use a variety of mold sizes, an increase in ingot butt practice in percentage of total metallic charge is apparent with larger size molds.

The total scrap used as a standard, therefore, is 3 per cent. miscellaneous and 1 per cent. ingot butts and condemned ingots. To this recovered scrap there should be added the metallic equivalent in the amount of slag consumed by the blast furnaces. This will vary considerably with practice at different plants and is especially limited by the phosphorus content of the pig iron which the open hearth can use to advantage. It may run from 0.0 per cent. to as high as 3.5 per cent. per ton of metallic charge and no standard can be used which will hold for the different conditions. No error is introduced, however, if one wishes to compare different practices either at one plant or different plants by assuming the same amount of metallics in slag recovered per ton of metallic charge. Whether this is 1 per cent., 2 per cent., or more, will not alter the accuracy of such comparisons.

Having thus established Total Losses and credited the metallic content in slag to arrive at Net Loss, one should add to the latter the total scrap recovered, which would include the metallics in slag if so recovered, and this would then represent Total Loss and Scrap. The total loss and scrap deducted from 100 per cent. gives the Ingot Yield.

Application of Method of Calculation

In a very exhaustive and interesting report, Kinney[10] furnishes a basis for using this method of calculation. Practice data for different type of heats are given, which will be used in the Fe to Si method of calculation. Since all these heats are balanced, and particularly since there is a balance for total silica, no error should obtain in the Fe to Si method of calculation and perfect checks should result. The data for the "Standard Iron, Low Silica Ore" are used, all other heats being calculated by the method illustrated. (See Tables 11, 12 and 13.)

[10] C. L. Kinney, Jr.: *Op. cit.*

TABLE 11.—*Calculation of Yields, "Standard Iron, Low Silica Ore;" Analysis of Materials Used*

	SiO_2, Per Cent.	Fe, Per Cent.	Si, Per Cent.	C, Per Cent.	Mn, Per Cent.	P, Per Cent.
Pig iron			0.75	4.30	1.00	0.200
Steel scrap				0.20	0.40	0.010
Ore (natural)	4.62	56.09	2.16			
Limestone	0.34		0.16			
Dolomite	1.32		0.62			
Fluorspar	1.12		0.52			
Slag (composite)	17.61	14.25	8.22			
Residual in bath				0.20	0.23	0.010

Slag ratio, Fe to Si: 1.73.

TABLE 12.—*Losses in Components of Basic Open-hearth Charge*

Type Losses		Fe in Ore, Scale, Etc.	Hot Metal or Pig Iron	Steel Scrap	Lime-stone	Dolo-mite	Spar
Metalloid losses	Carbon, per cent		4.10				
	Silicon, per cent		0.75				
	Manganese, per cent		0.77	0.17			
	Phosphorus, per cent		0.19				
Iron loss in slag (Fe to Si ratio), per cent		6.66	1.30	0.08	0.28	1.07	0.90
Spillage, oxides, foreign losses, per cent			0.50	0.40			
Miscellaneous losses, per cent		0.75	0.75	0.75			
Total losses, per cent		7.41	8.36	1.40	0.28	1.07	0.90

By accounting for the losses in components of the charge and multiplying this by the percentage of materials used, one arrives at the percentage of losses of materials used per ton of metallic charge. The ratio of Fe to Si in the slag is 1.73, or every unit of Si should be multiplied by 1.73 to obtain the iron lost in the slag, due to Si or SiO_2 entering the furnace. The loss in metalloids is the difference between that contained in the pig iron and scrap and the residual in the bath. The residuals are 0.20 per cent. carbon, 0.23 per cent. manganese, and 0.01 per cent. phosphorus. The spillage loss for iron is taken at 0.50 per cent.; the loss due to oxides in scrap, etc., 0.40 per cent., and the miscellaneous losses for all the metallic charge in bath, at 0.75 per cent. The loss in additions is, as explained previously, taken at 25 per cent. The total net loss is 6.11 per cent., total scrap 4.00 per cent., giving a total net loss and scrap of 10.11 per cent., or a yield of 89.89 per cent. This compares with the figure of 91.04 per cent. shown by Kinney. The difference of 1.15 per

cent. in the two yields is due to larger losses used as standards for miscellaneous losses, spillage on hot metal and oxides, dirt, etc., in scrap, in the Fe to Si slag ratio method of calculation. The yield of 91.04 per cent. is based on the allowance of 100 lb. iron lost in slag pockets, checker chamber dust, etc., which is the equivalent of 0.10 per cent. per ton of metallic charge. It is also based on a balance of metal in the bath, which would, therefore, not include the various losses used in the Fe to Si ratio method. By allowing for the difference of 0.65 per cent. miscellaneous losses, 0.50 per cent. for spillage and hot metal, 0.40 per cent. for scrap and the iron lost to SiO_2 content of dirt and scrap, a perfect check is obtained.

TABLE 13.—*Calculation of Basic Open-hearth Yields*

Materials	Percentage of Materials Used per Ton Metallic Charge	Percentage of Losses in Charge Components	Percentage of Loss per Ton of Total Metallic Charge
Fe in ore, scale, etc.	4.5	7.41	0.333
Hot metal	61.8	8.36	5.167
Steel scrap	33.3	1.40	0.466
Additions	0.4	25.00	0.100
Total metallic charge	100.0		6.066
Limestone	4.36	0.28	0.012
Dolomite	2.37	1.07	0.025
Fluorspar	0.28	0.90	0.003
Total losses			6.106
Metallics recovered in slag			
Net losses			6.11
Scrap recovered: Miscellaneous scrap			3.00
Condemned ingots and ingot butts			1.00
Metallics in slag			
Total scrap			4.00
Total net loss and scrap			10.11
Ingot yield			89.89
Total			100.00

It should be said that in actual operations, this type of charge would be more likely to give the lower yield of 89.89 per cent. The relative comparisons, as shown by Kinney, hold good, however, and do not disturb the accuracy of final differences in costs, as can be illustrated by applying the same method to all the heats. In so doing, we arrive at the following comparison (Table 14) and show also the ratio of Fe to Si which is an indication of iron loss in slag for various slag volumes. The difference in the ratio of Fe to Si in the various slags indicates the large

variation possible in this factor and the reason for being unable to apply any set Fe to Si ratio for all heats.

TABLE 14.—*Comparison of Yields*

	Kinney Yields, Per Cent.	Difference between Successive Yields, Per Cent.	Fe to Si Ratio Method, Per Cent.	Difference between Successive Yields, Per Cent.	Fe to Si Ratio in Slag
Standard iron-low SiO_2 ore.....	91.04		89.89		1.73
High manganese iron-low SiO_2 ore.	90.92	0.12	89.75	0.14	1.25
Standard iron-high SiO_2 ore.....	90.58	0.34	89.39	0.36	1.81
High-manganese iron-high SiO_2 ore.	90.39	0.19	89.20	0.19	1.44
High-phosphorus iron.....	90.11	0.28	88.94	0.26	1.73
Excess limestone.....	89.76	0.35	88.63	0.31	2.63
High-silicon iron.....	88.20	1.56	87.02	1.61	2.04

It will be noted that the maximum difference between the Fe to Si ratio method and the more complicated and exhaustive method of making exact balances, is 0.05 per cent. difference in yield, which can be explained by failure to carry out decimal places sufficiently far. This method is sufficiently accurate for practical purposes and may be considered a perfect check. Since it involves a minimum of analyses, it is convenient. Furthermore, this method is of considerable assistance in determining if an excessive amount of extraneous SiO_2, which normal analyses do not indicate, is being carried into the furnace. A recent investigation constituting a loss of 0.40 per cent. yield, disclosed a 20 per cent. greater silica content in the slag than the most careful SiO_2 balance could account for. That this is not unusual may be shown by reference to Diehl's paper,[11] which discloses a total "unaccounted for" SiO_2 ranging from 0.73 to 29.13 per cent., even when making provision for silica in runners and ladle linings.

Kinney's study[12] shows the influence of high-silicon iron, for example, on yields, and the same holds true in the case of high-silica materials. These larger losses, mainly from silicon in iron and silica in the ore, can be avoided only by a closer control of these factors. Within reasonable limits, this can be done.

An example is furnished to indicate the influence of increase in SiO_2 in ore used, assuming that a change is made from 6.5 per cent. SiO_2 and 80 per cent. Fe_2O_3 ore, to an ore containing approximately 10 per cent. SiO_2 and 76.5 per cent. Fe_2O_3. If the standard charge is the equival-

[11] *Op. cit.*
[12] *Op. cit.*

ent of 11.87 per cent. ore (natural) per ton metallic charge, then the total SiO_2 per ton of charge is 11.87 per cent. × 6.5 per cent. or 0.772 per cent. SiO_2, which is equivalent to 17.3 lb. SiO_2 per ton of charge. If the higher silica ore is used, the ore necessary becomes 12.41 per cent. per ton metallic charge. The SiO_2 involved is 12.41 per cent. × 10 per cent. = 1.24 per cent., or the equivalent of 27.8 lb. SiO_2, an increase therefore, of 10.5 lb. of silica per ton of charge. If the slag volumes are such as to produce 60 per cent. tapping slag and the desired ratio of CaO to SiO_2 in the silicate slag is 2.33, then the calculation becomes 10.5 × 60, or 6.30 additional pounds of SiO_2 and 6.30 × 2.33 divided by the lime content of limestone, say 53 per cent., gives an increase of approximately 26.7 lb. of limestone. If the silicate proportion of the slag shows a ratio of approximately 5.3 to the SiO_2 content thereof, the total increase in slag volume is 5.3 × 6.30 or 33.4 lb. of slag per ton of charge. Further, if the slag contains 16 per cent. iron, this is the equivalent of an additional loss of 5.3 lb. of iron per ton of charge, or 0.24 per cent. in yield.

In usual practice, provision is made for the normal variations of silicon content of the iron by charging sufficient limestone. Where excessive fluctuations occur, excessive limestone charges are common, resulting in large slag volumes and high metallic losses, with consequent decrease in yields. Unless calculated, one fails to note the decided decrease in yield resulting from high metallic losses in slag for any given charge, due to high-silicon iron or high-silica materials. For example, one plant tapping approximately 95-ton heats, charges about 18,000 lb. of limestone for a silicon in iron running 0.90 to 1.15 per cent. and adds about 1800 lb. when the silicon goes to 1.35; 3600 lb. when the silicon goes to 1.55; and 5400 lb. when it goes to 1.75. The decrease in yield is quite obvious with the higher silicon content iron, apart from other important losses in economy.

The Fe to Si ratio method when applied to plants using recarburizer iron, is changed to some extent in order to take care of the lower metalloid losses in that part of the total pig iron charge furnished by the recarburizer metal. One must make allowances for the lower metalloid losses on the recarburizer, consistent with the practice at the plant. The other factors, spillage, miscellaneous, etc., are applied in the same manner as shown for hot metal.

Duplex Operations

In applying the method to duplex operations, which are a combination of acid bessemer and basic open hearth, the same system can be applied, with the exception that the spillage allowance on the blown metal is higher because of the increased number of transfer ladles. This factor is 0.80 per cent. instead of the 0.50 per cent. allowed on ordinary hot metal charges. The metal used for blowing in the following comparison, is a

combination of low-manganese basic and standard bessemer iron. The bessemer slag resulting is as follows:

FeO, Per Cent.	Fe_2O_3, Per Cent.	MnO, Per Cent.	SiO_2, Per Cent.	CaO, Per Cent.	MgO, Per Cent.	Al_2O_3 and TiO_2, Per Cent.
16.00	2.03	14.62	61.40	0.72	0.75	3.72

The average yield of blown metal is 91.3 per cent., and for our purposes a recovery of 1.0 per cent. scrap is made as well as 1.0 per cent. for Fe in slag, shot and spittings later consumed at blast furnaces. Therefore, per ton of blown metal the scrap is 1.1 per cent. and Fe in slag, spittings, etc., 1.1 per cent., the loss 7.3 per cent., or a total loss and scrap of 9.5 per cent. per ton of blown metal. While the amounts in actual practice may differ from these figures, they nevertheless serve to indicate the degree of difference in duplex yields with varying amounts of blown metal

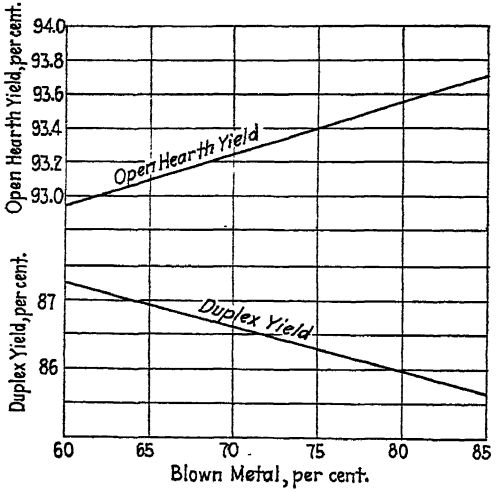


FIG. 2.—INGOT YIELD IN DUPLEX BASIC OPEN HEARTH; VARYING AMOUNTS OF BLOWN METAL.

used. It will be assumed that the same type steels are made and have the same residuals in the bath. In actual practice this does not occur, but the qualification introduces no error in the relative differences illustrated. This would mean more ore on the lower blown metal percentages and more manganese or spiegel in the bath on the higher. The error introduced is negligible, the curves shown (Fig. 2) being changed from straight lines to a curve with an extremely long radius, the maximum error being 0.10 per cent. on all heats.

Since the same characteristics are desired in the slag, one can readily calculate the yields obtained in the open-hearth department (only), as well

as the combination or duplex yield. The losses and scrap for open hearth are figured and to this the losses and scrap per ton blown metal are added. Since none of the open-hearth slag is consumed in blast furnaces, the credit is nil, but the total scrap will include the amount of Fe in slag, spittings, etc., credited to bessemer, and in proportion to the percentage of blown metal used. The basis used is 80 per cent. blown metal, the balance hot metal, cold iron, scrap, etc. The complete details of slags, analysis of materials, and proportions per ton metallic charge are shown in Tables 15, 16 and 17. It will be noted that for the open hearth (only) the calculated yield is 93.55 per cent., total scrap 3.00 per cent., and loss 3.45 per cent. The loss and scrap per ton blown metal is 1.1 per cent. scrap, plus 1.1 per cent. Fe in slag, plus 7.3 per cent. loss or a total of 9.5 per cent. Adding the loss and scrap of open hearth (per ton charge) to that of blown metal (per ton blown metal), the result is as follows, *viz.:* 6.45 per cent. (open-hearth loss and scrap) + [80 per cent. × 9.5 per cent. (bessemer loss and scrap)] or a duplex total loss and scrap of 14.05 per cent. The yield is therefore 85.95 per cent. The scrap constituents are calculated in the same manner. The curves (Fig. 2) demonstrate the decreased yield obtained in duplex operations with increased amounts of blown metal, based on assumptions previously explained. At the same time the open-hearth yield shows a proportionate increase with increased blown metal charges. (For a sample calculation see Table 18.)

TABLE 15.—*Analysis of Materials Used*

	SiO_2, Per Cent.	Fe, Per Cent.	Si, Per Cent.	C, Per Cent.	Mn, Per Cent.	P, Per Cent.
Pig iron (hot and cold)..			1.30	4.20	0.80	0.17
Blown metal.....				0.04	0.10	0.18
Steel scrap.....				0.15	0.43	0.02
Limestone.....	1.00		0.47			
Dolomite.....	2.00		0.93			
Fluorspar.....	4.90		2.29			
Slag.....	12.72	19.07	5.94			
Residual in bath.....				0.08	0.15	0.02

Slag ratio, Fe to Si: 3.21.

The following represents the analysis of normal open-hearth slags produced under the conditions named:

SiO_2, Per Cent.	Fe_2O_3, Per Cent.	FeO, Per Cent.	MnO, Per Cent.	CaO, Per Cent.	MgO, Per Cent.	P_2O_5, Per Cent.	Al_2O_3 and TiO_2, Per Cent.	S, Per Cent.
12.72	6.62	18.56	7.37	42.41	7.03	3.74	1.45	0.18

TABLE 16.—*Losses in Components of Basic Open-hearth Charge (Duplex Operations)*

Type Losses, Per Cent.		Blown Metal	Cold Iron	Hot Metal	Steel Scrap	Lime-stone	Dolo-mite	Spar
Metalloid losses	Carbon	+.04	4.12	4.12	0.07			
	Silicon		1.30	1.30				
	Manganese	+.05	0.65	0.65	0.28			
	Phosphorus	0.16	0.15	0.15				
Iron loss in slag (Fe to Si ratio)			4.17	4.17	0.15	1.51	3.00	7.35
Spillage, oxides, foreign losses		0.80		0.50	0.40			
Miscellaneous losses		0.75	0.75	0.75	0.75			
Total losses		1.62	11.14	11.64	1.65	1.51	3.00	7.35

TABLE 17.—*Calculation of Basic Open-hearth Yields (Duplex Operations)*

Materials	Percentage of Materials Used per Ton Metallic Charge	Losses in Charge Components	Percentage of Loss per Ton of Total Metallic Charge
Blown metal	80.0	1.62	1.296
Hot metal	12.0	11.64	1.400
Cold iron	3.3	11.14	0.368
Steel scrap	4.0	1.65	0.066
Additions	0.7	25.00	0.175
Total metallic charge	100.0		3.305
Limestone	5.55	1.51	0.046
Dolomite	1.53	3.00	0.084
Fluorspar	0.15	7.35	0.011
Total losses			3.446
Metallics recovered in slag			
Net losses			3.45
Scrap recovered: Miscellaneous scrap			2.00
Condemned ingots and ingot butts			1.00
Metallics in slag			
Total scrap			3.00
Total net loss and scrap			6.45
Ingot yield			93.55
Total			100.00

Table 18 shows details of product, scrap and loss for the duplex operation for each percentage of blown metal, *i. e.*, combination acid bessemer and basic open hearth. The yield for open hearth is also shown, as well as the scrap and loss for the same conditions.

TABLE 18.—*Practice Data for Duplex Operations*

Details	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Blown metal	60	65	70	75	80	85
Open-hearth (only) yield	92.95	93.10	93.25	93.40	93.55	93.70
Total scrap	3.00	3.00	3.00	3.00	3.00	3.00
Total loss	4.05	3.90	3.75	3.60	3.45	3.30
Duplex yield	87.25	86.92	86.60	86.27	85.95	85.62
Fe in slag, shot, etc. (Bessemer)	0.66	0.72	0.77	0.82	0.88	0.93
Miscellaneous scrap (Bessemer)	0.66	0.72	0.77	0.82	0.88	0.93
Open hearth miscellaneous scrap	2.00	2.00	2.00	2.00	2.00	2.00
Open-hearth condemned ingots and butts	1.00	1.00	1.00	1.00	1.00	1.00
Total scrap	4.32	4.44	4.54	4.64	4.76	4.86
Total loss	8.43	8.64	8.86	9.09	9.29	9.52

Influence of Proportion of Pig Iron Charges on Ingot Yields

Fig. 3 is a characteristic curve showing the performance of one stationary open-hearth plant with varying amounts of pig iron and scrap

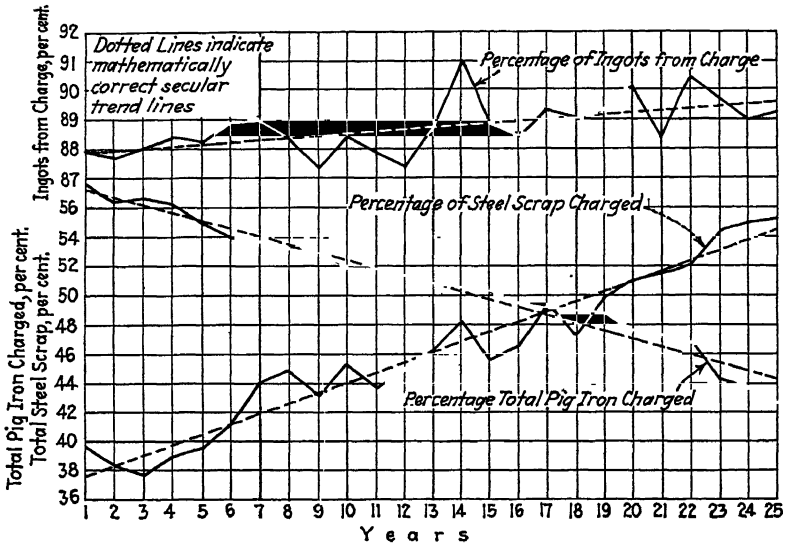

Dotted Lines indicate mathematically correct secular trend lines
Percentage of Ingots from Charge
Percentage of Steel Scrap Charged
Percentage Total Pig Iron Charged
Ingots from Charge, per cent.
Total Pig Iron Charged, per cent.
Total Steel Scrap, per cent.
Years

FIG. 3.—CHARACTERISTIC BASIC OPEN-HEARTH YIELD WITH DIFFERENT PERCENTAGES OF PIG IRON.

over a period of 25 years. It will be noted that in spite of the multitude of variations possible, such as analyses of materials, overloading furnaces, types of steel, etc., a definite relation exists between pig charge and yield. Such curves can be further extended to show influence of

percentage pig iron charged for more equal conditions. In such a comparison the curve will have a very definite aspect or trend.

Fig. 4 represents such a condition. "Equal conditions," in the sense in which used here, refers to the lack of extreme variations over short periods as compared to a curve (Fig. 3) covering a period of 25 years. It represents actual slag proportions and analyses, analysis of materials in metallic charge and proportions used per ton metallic charge for a period of approximately three months. It is assumed that for a 50 per cent. hot metal charge, the standard of 3 per cent. miscellaneous scrap and 1 per cent. condemned ingots and ingot butts obtains. Therefore, the miscellaneous scrap for lower or higher percentages used is adjusted

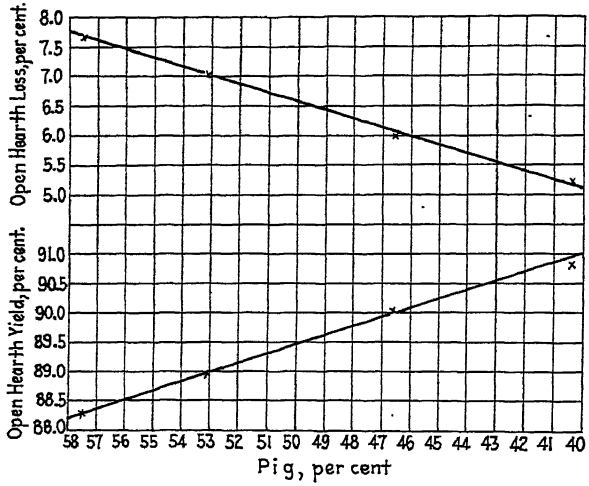


FIG. 4.—BASIC OPEN-HEARTH YIELDS; VARYING PERCENTAGES OF PIG IRON, EQUAL CONDITIONS.

to take care of standard of 0.50 per cent. iron scrap produced per ton hot metal. The curve clearly demonstrates the influence of percentage pig charges on yields for "equal conditions." The same study can be employed to denote possible yields for any steel with varying pig charges, or same charge for different steels. Table 19 shows the practice obtaining for various pig percentages. The calculations are made in the usual manner for Fe to Si slag ratio, etc.

TABLE 19.—*Practice Data for Stationary Open-hearth Furnaces*

Pig Iron, Per Cent.	40.4	46.6	53.1	57.5
Yield, per cent.....	90.82	90.04	88.96	88.27
Scrap, per cent.....	3.95	3.98	4.02	4.04
Loss, per cent.....	5.23	5.98	7.02	7.69

Slags

It is evident that the plant which is devoted principally to the manufacture of low-carbon steels, say 0.10 per cent. carbon or under, will for any given analysis of materials or charge, show a lower yield than plants where higher carbon steels are made. This is due to the rapid increase in slag volume and metallic oxide as the low-carbon ranges are approached, since the lower carbon heats require higher iron oxides. Some interesting work done by Herty,[13] discloses the relation between carbon and iron oxide for different temperatures, and shows the characteristic influence at equilibrium conditions. While such conditions rarely obtain in actual practice, they illustrate the possibilities of reducing losses by finishing at a higher temperature in the furnace, within limits imposed by existing conditions, and holding heats in the ladle, the latter practice being considered by some conducive to better quality steel. It is shown "(1) a small increase in FeO in the slag brings about a large drop in carbon content of the metal when the carbon is high, say, 0.40 per cent. carbon or over; (2) a large increase in FeO in the slag is necessary for a small drop in carbon at low-carbon contents, 0.10 per cent. carbon and under; and (3) increase in temperature from 2800° to 3000° F. causes a 75 per cent. reduction in carbon content with no increase in the iron oxide content of the slag." These considerations are of interest to open-hearth operators and actual determinations of such possibilities should prove of interest when made on a practical scale.

While one can empirically determine satisfactory slag component ratios for individual plants, based on those types yielding satisfactory results over long periods of time, such standards cannot be applied to a group of plants, without introducing serious errors in the determination of yields. Apart from the great variety of analyses of materials, differences in charge ratios, and final slags, the element of run-off slags introduces a large possible error. Table 20 indicates to what extent final slags may vary when applied to plant practices, each plant making a variety of steels, and the slags representing average conditions. Some obtain run-off slags and others do not. Some represent cold iron plants with high scrap charges, many recarburizing with hot metal, while some are devoted to the lower carbon steels, say 0.40 per cent. C down. The last four denote individual heats.

It will be noted that these slags show a perceptible difference in basicity, and Fe to Si ratio, the result of practice followed, which in turn is based on range of carbon steels made and type of slag which has been found most satisfactory to produce desired results. It is obvious, therefore, that one must use actual analyses of slags as produced which

[13] The Physical Chemistry of Steel Making; Solubility of Iron Oxide in Iron. *Bull.* 34, *Min. and Met. Investigations*, Carnegie Inst. of Tech.

have been found desirable for the conditions or steel desired. One can then empirically calculate slags as demonstrated by Kinney,[14] by dividing into a silicate slag, and a phosphate slag. The silicate slag is assumed to hold the phosphate slag in solution, which is taken at $Ca_4P_2O_9$. The phosphate and silicate slags naturally give the total slag. Where no run-off slag occurs, this method can be used to advantage. However, the run-off slag will cause a serious error in calculating yields in this manner, unless provision is made, this being done by assuming the proportion of run-off slag. Table 21 shows some typical analyses of run-off slags, which are given in the order of those previously presented, that is, they represent the run-off slags for the first 10 analyses in Table 20.

TABLE 20.—*Final Tapping Slags*

Slag No.	SiO_2, Per Cent.	P_2O_5, Per Cent.	CaO, Per Cent.	MgO, Per Cent.	Fe, Per Cent.	Mn, Per Cent.	Fe to Si Ratio	Phosphate Slag, Per Cent.	Silicate Slag, Per Cent.	Silicate Slag to SiO_2, Ratio
1*	17.59	2.07	39.30	7.00	15.65	6.10	1.91	5.34	94.66	5.38
2*	19.03	1.85	41.10	7.30	13.50	5.58	1.52	4.77	95.23	5.00
3*	19.11	1.90	40.20	7.36	14.25	5.26	1.60	4.90	95.10	4.98
4*	16.22	1.95	43.68	6.42	17.52	5.51	2.31	5.03	94.97	5.85
5*	17.08	2.11	41.80	6.45	17.68	5.31	2.22	5.44	94.56	5.54
6*	17.80	2.21	41.79	6.50	14.86	5.96	1.79	5.70	94.30	5.29
7*	17.30	2.11	43.67	6.40	15.37	4.17	1.90	5.44	94.56	5.46
8*	16.30	2.08	40.51	7.12	17.66	5.76	2.32	5.37	94.63	5.80
9*	19.37	2.16	39.99	8.12	12.36	7.10	1.33	5.57	94.43	4.76
10*	17.05	1.51	46.35	8.00	11.68	5.65	1.47	3.90	96.10	5.64
11	17.25	2.91	46.80	6.43	12.00	5.60	1.49	7.51	92.49	5.36
12	16.00	2.10	42.50	6.40	17.10	6.20	2.29	5.56	94.44	5.96
13	18.00	2.30	41.00	6.45	14.80	7.73	1.76	5.93	94.07	5.23
14	15.00	1.75	45.50	5.50	16.29	6.20	2.33	4.52	95.48	6.36
15	15.58	3.66	48.00	6.02	10.62	7.56	1.46	9.44	90.56	5.81
16	19.42	2.76	50.83	6.18	8.87	3.97	0.98	7.12	92.88	4.78
17	15.86	3.71	47.63	6.00	10.83	7.08	1.46	9.57	90.43	5.70
18	22.15	1.43	48.28	5.35	8.21	4.38	0.80	3.69	96.31	4.35

* Operations with run-off slags.

TABLE 21.—*Run-off Slags*

Slag No.	SiO_2, Per Cent.	P_2O_5, Per Cent.	CaO, Per Cent.	MgO, Per Cent.	Fe, Per Cent.	Mn, Per Cent.	Fe to Si Ratio	Phosphate Slag, Per Cent.	Silicate Slag, Per Cent.	Silicate Slag to SiO_2, Ratio
1	24.50	2.30	16.38	5.60	24.00	9.60	2.10	5.93	94.07	3.84
2	24.14	2.16	14.68	4.20	27.25	9.00	2.42	5.57	94.43	3.91
3	24.37	2.20	15.64	3.95	27.60	9.10	2.43	5.68	94.32	3.87
4	27.41	2.04	27.75	8.41	23.45	9.95	1.83	5.26	94.74	3.46
5	20.92	2.57	22.15	4.25	26.91	9.20	2.76	6.63	93.37	4.46
6	21.35	2.54	19.20	7.14	25.39	9.30	2.75	6.55	93.45	4.38
7	24.39	2.58	19.05	6.49	24.80	6.90	2.18	6.66	93.34	3.83
8	24.76	2.35	17.77	5.82	24.20	11.15	2.09	6.06	93.94	3.79
9	22.72	2.62	17.43	7.68	26.25	9.45	2.48	6.76	93.24	4.10
10	23.19	2.04	21.11	7.67	22.92	10.85	2.11	5.26	94.74	4.09

[14] C. L. Kinney, Jr.: *Op cit.*

It will be observed that while the run-off slags show variations, these are not of the same degree as obtains for final slags, due to the considerable changes that occur in final slags with ranges of carbon desired. The run-off slags contribute a sensible amount of loss of iron and manganese, the proportion varying almost directly with slag volume involved. For example, in the first three analyses the run-off constitutes 28.1, 37.4, and 39.8 per cent., respectively, the total slag volumes being 404, 409, and 420 lb. per ton of ingots, an average of approximately 18.5 per cent. per ton metallic charge. The proportion of iron losses by run-off and tapping slags are shown as follows:

TABLE 22.—*Loss of Iron in Slags, Percentage per Ton of Metallic Charge*

Slag No.	Run-off	Tap	Total	Proportion of Fe Loss in Run-off
1	1.25	2.04	3.29	38.0
2	1.89	1.57	3.46	55.0
3	2.02	1.67	3.69	55.0

While losses of metallics in run-off slags as indicated by the Fe loss, will vary considerably for plants using high pig and ore charges, and the above (Table 22) cannot be considered applicable to all plants, it is obvious that the use of run-off slags inherent to this type of charge, is productive of large losses and a decrease in ingot yield. How far these losses can be corrected is largely a problem of ore beneficiation and the limiting commercial amounts to be charged. Run-off slags are incidental to high pig iron charges and rarely occur in practice where proportion of pig iron and scrap are equal, or where the latter is greater. Where run-off slags are used, their main purpose is to remove the excess acid constituents which thereby causes the loss of some part of the lime. The balance is available for later stages of the heat. It is apparent that the extent of such preliminary cleansing will largely determine the amount of metallics lost.

The extent to which iron losses accompanying excessive slag volumes may be decreased, is largely a matter for individual plant study. Due to analytical vagaries of materials used, furnaces must always be charged with limestone that will afford an ample measure of security. At times this may be carried to excess with unnecessarily high losses of metallics. It is in this field of yield investigation that thus far we are forced to use empirical methods largely. Whether or not to carry excessive slag volumes, costly in metallic losses, fuel and tonnage, in order to avoid occasional off-phosphorus heats, is a question that can be answered only by careful study of individual conditions. Colclough[15] has made some

[15] T. P. Colclough: The Constitution of Basic Slags; Its Relation to Furnace Reactions. *Jnl.* Iron and Steel Inst. (1923) **107**, 267.

interesting determinations which indicate that melting slags are essentially composed of molecules of phosphate lime ($4CaO, P_2O_5$) and molecules of monosilicate ($2RO, SiO_2$), in which RO may be CaO, MgO, MnO, or FeO, as well as Fe_2O_3. One can obtain some measure of the amount of bases necessary to give satisfactory results in normal practice from this basis.

In Table 23, nine heats are shown which varied in carbon content from 0.08 to 0.21 per cent. The initial ore charge was between zero and 11 per cent., and the average manganese content of the iron 2.30 per cent. The molecular percentages are figured by dividing the weight per cent. of the components in slag by the molecular weight. For example, in heat 1, the SiO_2 content is 10.52 per cent.; then $\frac{10.52}{60} = 17.53$ per cent. written 0.1753. The base necessary for this would be $2ROSiO_2$ or 0.3506. The P_2O_5 in this slag was 2.08 per cent., which gives the following: $\frac{2.08}{142} = 0.01465$. The CaO for $4ROP_2O_5$ gives $4 \times 0.01465 = 0.0586$. Other calculations are made in the same manner. Table 23 indicates that one may reasonably conclude that given a molecular percentage of CaO equal to the sum of the molecular percentages of SiO_2 and P_2O_5, phosphorus elimination is satisfactory and no appreciable reversion of this element will take place if the slags are sufficiently oxidizing. Two factors are therefore necessary; *viz.*, excess base and sufficient iron oxide to satisfy the equilibrium conditions of the dephosphorizing reaction.

Dichmann[16] in speaking of phosphorus reversion states "it is apparent that the re-entry of phosphorus into the metal accompanies an increase in silica content of the slag, or carries too far the removal of iron oxide from the same, thereby creating more than normal efforts on the part of the reducing agents to satisfy their affinity for oxygen."

Herty[17] expresses something of the same thought in regard to phosphorus elimination in a statement that "for a given amount of phosphorus in the charge and a given slag and metal weight, the extent of elimination will depend on the concentration of iron oxide and available base in the slag and on the temperature." Since the reactions, in which phosphorus is eliminated, are strongly exothermic, this elimination takes place more rapidly at lower temperatures.

Conclusion

In conclusion, it should be stated that for any given charge and desired slag analysis or steel, there is a definite yield, varying largely with scrap produced and miscellaneous losses. Because of the multitude of

[16] C. Dichmann: *Op. cit.*

[17] C. H. Herty, Jr.: Chemical Equilibrium of Manganese, Carbon, and Phosphorus in the Basic Open-hearth Process. *Trans.*, A. I. M. E. (1926) **73**, 1107.

TABLE 23.—*Molecular Analysis of Slags; Basicity Ratio*

Heat No.	FeO, Per Cent.	MnO, Per Cent.	CaO, Per Cent.	SiO_2, Per Cent.	P_2O_5, Per Cent.	Molecular Analysis of Slags, Per Cent.							Limestone, Lb. Ton Ingots	Residual Manganese, Per Cent.	Analysis of Final Steel, Per Cent.		
						P_2O_5	$\frac{4RO}{P_2O_5}$	SiO_2	$\frac{2RO}{SiO_2}$	Total Molecular Base	Molecular CaO Present	Excess CaO			C	P	S
1	18.79	12.42	42.05	10.52	2.08	0.01465	0.0586	0.1755	0.351	0.4096	0.751	0.3414	140	0.28	0.21	0.010	0.018
2	19.27	14.00	38.19	11.25	1.90	0.01338	0.0535	0.1875	0.375	0.4285	0.682	0.2535	139.5	0.25	0.18	0.008	0.019
3	15.57	9.14	41.79	14.94	2.00	0.01340	0.0536	0.2490	0.498	0.5516	0.746	0.1944	214	0.19	0.13	0.010	0.028
4	14.99	16.42	37.25	15.42	2.36	0.01663	0.0665	0.2570	0.514	0.5805	0.665	0.0845	108	0.30	0.20	0.016	0.029
5	11.46	13.17	42.78	13.20	2.31	0.01628	0.0651	0.2200	0.440	0.5051	0.765	0.2599	143	0.29	0.21	0.014	0.024
6	11.26	11.84	41.47	14.38	2.00	0.01340	0.0536	0.2395	0.479	0.5326	0.750	0.2174	163	0.29	0.15	0.013	0.019
7	11.21	12.76	42.41	14.80	2.61	0.01837	0.0735	0.2465	0.493	0.5665	0.759	0.1925	106	0.26	0.11	0.010	0.025
8	11.71	14.89	40.75	16.26	2.36	0.01663	0.0665	0.2710	0.542	0.6085	0.728	0.1195	108	0.37	0.13	0.022	0.022
9	12.30	18.76	35.80	18.72	2.20	0.01550	0.0620	0.3120	0.624	0.6860	0.639	−0.0470	119	0.33	0.13	0.031	0.029
Average..	14.06	13.71	40.28	14.39	2.20	0.01535	0.0614	0.2455	0.491	0.5410	0.721	0.1795	137.8	0.284			

different losses possible in converting a metallic charge into steel ingots, it is desirable to investigate all sources of probable loss. To ascertain the cause of losses, it is necessary occasionally to conduct carefully controlled heat tests. After obtaining some idea of the amount of metallics lost in the different parts of the operation, one can empirically develop a method of calculating possible yields for any charge or type of steel based on the Fe to Si ratio in slags, which will give a very satisfactory check on operations. It does not follow, though, that the best yield will give the lowest cost ingots. This will depend entirely on the relative prices of materials making up the gross metallic charge for equal scrap recovery. There must also be considered the difference in cost in converting any type of metallic charge to ingots. In addition, where plants are physically handicapped in charging large amounts of scrap, thus slowing up production and adding in obvious ways to the cost of conversion, it may be found desirable to forego the use of the cheaper metallic mixture. The lower yield with higher ore and pig charges does not, therefore, necessarily mean higher ingot cost in actual practice, since the inexpensive iron in the ore may give a lower cost for the mixture, thereby offsetting the disadvantages of lower yields. Therefore, it is apparent that the open-hearth yield does not necessarily determine the charge to be used, but that blast-furnace, open-hearth and metal-market conditions will also largely govern the choice.

While the physical factors involved in losses may be determined with desired accuracy, the metallurgical phases require more comprehensive investigation of the physical chemistry of the slag and metal than have been heretofore made.

This paper is presented with the hope that it may stimulate a more comprehensive and thorough study of the question of basic open-hearth yields, an important phase of steel-mill operation and too often accepted as not susceptible to improvement. We wish to express our appreciation to our colleagues for their many helpful suggestions and assistance in the preparation of this paper.

DISCUSSION

C. E. MEISSNER, Carteret, N. J.—What is the practical application of the work in Mr. King's paper?

C. D. KING.—It enables the operator to determine whether or not he is getting the maximum possible ingot yield for any charge or condition. It gives him a check on most desirable fuel from standpoint of total economy, most desirable charge from a standpoint of speed, total output, and finally it makes it possible to judge when to use maximum pig iron charge or maximum scrap charge. Whether a decrease in yield with higher percentage pig charges is discounted by cheaper total ingot cost can be calculated in advance. In short, an intelligent check is furnished the operator in the guidance of his charges and operations.

Physical Chemistry of Steelmaking

ROUND TABLE

(New York Meeting, February, 1929)

AN informal discussion on the application of physical chemistry to steelmaking was held during the Annual Meeting of the Institute in February, 1929. Alexander L. Feild presided. In opening the session, Mr. Feild said:

We are all familiar with the cooperative mining and metallurgical studies that were begun in 1920 by the U. S. Bureau of Mines, the Carnegie Institute of Technology, and the Mining and Metallurgical Advisory Boards, and in particular with the work on the physical chemistry of steelmaking which was launched under the technical direction of Dr. C. H. Herty, Jr., in May, 1926. It was this work at Pittsburgh more than anything else that was the immediate cause of the formation within the Institute of a committee on the physical chemistry of steelmaking.

During the latter part of 1927 a small group of Institute members interested in the general subject of the physical chemistry of steelmaking undertook the organization of a subcommittee within the Iron and Steel Committee, to foster an active interest in this comparatively new field among the Institute membership and to obtain papers for publication in the TRANSACTIONS, covering the various phases of the general subject. This plan was conceived by C. E. Meissner, to whose active efforts at the outset as well as during the past year is largely due whatever measure of success the plan has thus far attained. The subcommittee, now a committee of the Iron and Steel Division, was recognized and formally made a part of the Institute's organization at the February, 1928, meeting.

As originally organized and as constituted during the past year the committee has been made up as follows: C. H. Herty, Jr., C. D. King, A. B. Kinzel, John Johnston, C. E. Meissner, L. F. Reinartz, R. B. Sosman, and A. L. Feild, Chairman. Dr. C. H. Herty, Jr. has just been elected chairman for the coming year and C. E. Meissner has been reelected as secretary. From the outset it has been the settled policy of the committee to make membership an annual rather than a permanent matter and to reconstitute in part the membership of the committee each year by dropping a certain number of members and adding new members. In view of the fact that the work of the committee is still in a

somewhat formative stage, it was agreed that the change this year should consist only in an increase in membership from 8 to 12.

While the majority of those present undoubtedly have a clear idea of the general scope and meaning of the phrase "physical chemistry of steelmaking" and are aware of the keen interest and enthusiasm which is being shown today by the iron and steel fraternity in all that the term embraces, it may nevertheless be worthwhile at this juncture to indulge in a few generalizations and to lay down several bench-marks important from the historical viewpoint.

Steelmaking is a word which may be variously defined, but for our purposes it may be considered as covering the *making* of steel from its raw materials rather than those subsequent operations, mainly thermal and mechanical, by which the steel is brought into the final shape and condition desired. Viewed in this way, steelmaking is essentially a branch of chemical engineering. Underlying every branch of engineering is to be found one or more sciences upon whose application the particular engineering technology in question is based. The underlying science is commonly designated as a pure or theoretical science to distinguish it from the *applied* science of which engineering consists. So far as steelmaking itself is concerned the science of chemistry is synonymous with physical chemistry, and it is for this reason that Sir Robert Hadfield, in an address delivered in 1925, referred to physical chemistry as the fundamental science of steelmaking.

The question naturally arises as to why we are standing today at the very threshold of the application of physical chemistry to the metallurgy of steel when, from the industrial and economic standpoint, steel manufacture has over a period of years been an increasingly dominant factor in our civilization. The answer is twofold. First, the advent of the Bessemer and open-hearth processes of manufacture antedated the birth of physical chemistry; and second, little if any effective contact has occurred until recently between the trained physical chemist and the experienced metallurgist. As might be expected in such a situation, realization of the fundamental relation between physical chemistry and steelmaking was itself a slow growth. The tardiness of such a realization was without doubt largely due to the inherent difficulties which attend physicochemical research at steelmaking temperatures as well as by the peculiarly stubborn qualities of the element iron as a medium for exact and systematic experimentation, especially above its melting point.

The importance of physical chemistry in steelmaking was brought forcibly to the attention of the iron and steel world in Juue, 1925, when it was made the subject of a general discussion, with original papers, at a joint meeting of the Faraday Society and the British Iron and Steel Institute. It need not be said that the splendid work of Dr. Herty and his associates at Pittsburgh has been the most immediate and important

factor in stimulating an active interest in this field, in this country at least. A measure of credit is due to our Institute because of the fact that the present discussion, together with the other activities of our committee during the past year, represents the first attempt of an engineering society to build a permanent and systematic part of its activities within this highly important field.

I have referred to the former absence of contact between physical chemist and metallurgist. During a considerable period, extending roughly from 1855, when Bessemer received his first patent, until 1925, when the joint meeting was held in England, important but exceedingly laborious progress was made toward an understanding of the true nature of the steelmaking processes. Such progress came about, for instance, when some metallurgical genius would acquire either intuitively or by intent a certain understanding of the operation of physicochemical principles, or when some trained physical chemist would turn his attention more or less casually to brief consideration of steelmaking reactions.

DISCUSSION

(The paper by C. H. Herty, Jr., beginning on page 260, is a part of this Round Table.)

A. L. Feild, New York, N. Y.—That period happily has passed when the metallurgist worked without a knowledge of physical chemistry, without anything but the vaguest idea of what goes on in the steel furnace. The purpose of this meeting is not primarily to discuss original contributions to the subject—we have had those in the past at our meetings—but to attempt, by way of a general discussion, to come to some general understanding about what steelmaking consists of from the chemical viewpoint. All of us have some idea what it is, but it is difficult to get two men to agree on all points when speaking about the open hearth, for instance, even on fundamentals. So Mr. Reinartz has prepared a list of questions which Mr. King will present. They cover the open-hearth process from the beginning of the charging until solidification in the mold. Occasionally Dr. Herty will answer the questions.

As you undoubtedly know, your committee is composed of open-hearth men and physical chemists. We hope some day the two terms will mean only the difference between the proponents of a science and of an applied science.

C. D. King, New York, N. Y.—I have grouped Mr. Reinartz' questions according to the charge, the making of the steel, the action in the ladle, and the final solidification in the mold. The opening questions, which have a very important bearing on open-hearth practice, have to do with pig-iron composition. The first question is: What influence has the silicon content of pig-iron on the removal of sulphur or phosphorus from the steel?

Influence of Silicon Content of Pig Iron on Removal of Sulfur or Phosphorus from Steel

C. H. Herty, Jr., Pittsburgh, Pa.—This question gets down to the basis of the basic open-hearth process. The basic open-hearth process is used primarily because phosphorus and sulfur can be eliminated from steel. This is effected by formation of calcium phosphate and calcium sulfide, both of which are insoluble in the metal and

enter the slag where they are held by excess base. The reason they are held is one of the primary laws of physical chemistry, the law of mass action. If there are two substances, A and B, reacting to give C and D, $A + B \rightleftharpoons C + D$ and if that reaction does not go all the way to completion, the law of mass action states that at equilibrium C and D are being formed from A and B as fast as A and B are being formed from C and D, and there is no change in the concentration of any one of the four reacting substances. The relationship between the four reacting substances at that time is expressed as

$$K = \frac{(C)(D)}{(A)(B)}$$

where (A) is the concentration of A, (B) the concentration of B, etc., and where K is the equilibrium constant. Actually the concentration terms should be expressed as *activities*, but until we learn more of the relation between concentration and activity of the substances encountered in steelmaking, we must use concentrations as the quantities in the equation above.

Take the reaction of sulfur, for instance. It may be written $FeS + CaO \rightleftharpoons CaS + FeO$. At equilibrium

$$K = \frac{(CaS)(FeO)}{(FeS)(CaO)},$$

which means that K is equal to the concentration of CaS in the slag multiplied by the oxidizing power of the slag, divided by the concentration of sulfur in the metal, times the concentration of available base in the slag. In order to get the reaction to go far enough, there must be excess base, CaO, to throw the reaction to the right and keep it there. So, in addition to having lime present, there must be excess of lime because the term (CaO) designates the amount of lime over and above that required to satisfy the silica and P_2O_5 in the slag. This brings us to the second point; that is, why do you have to have silicon in iron? If it were possible to make pig iron without silicon, would it be desirable?

I think the answer is this: The function of a slag in an open-hearth process is not simply to protect the metal from oxidation, but to control the rate at which the metal is oxidized. We could put on a slag of practically 100 per cent. iron odixe, by loading the furnace with ore and eliminating carbon rapidly, but we would probably freeze the heat. We can run a furnace without ore additions and simply allow the slag slowly to oxidize from the oxidiation of the scrap and carry on a very slow operation. But by having the proper slag volume and controlling the amount of iron oxide in the slag, we can regulate the oxidation of the metal, and that is extremely important in the case of rimming steels where there must be a certain amount of gas.

So there must be silicon in the iron to form a basis for a slag where iron oxide is held in solution and the rate of elimination of impurities and evolution of gas from the metal are controlled.

As far as sulfur and phosphorus are concerned, the effect of silicon is this: If a given amount of lime is charged and the silicon in the pig iron increased, the CaO would be lowered and sulfur and phosphorus could not be eliminated as readily. If the silicon in the pig iron is lowered, the excess base is increased and further elimination of sulfur and phosphorus effected, except that if the silicon gets too low a slag so thick and inactive is obtained that it takes too long to eliminate sulfur, phosphorus and carbon.

What is done is to strike a balance between the amount of silicon in the charge and the amount of lime charged, to give the required elimination of sulfur and phosphorus and speed in working.

C. D. KING.—What disadvantage attends the use of high-silicon iron, say 1.5 per cent. and low-silicon iron, 0.5 per cent.?

C. H. HERTY, JR.—There are two or three points to consider. If high-silicon iron is used when charging for a normal silicon iron—for instance, suppose you have charged a heat to take care of pig iron at 1 per cent., and you get 1.50 or 1.75 per cent. silicon iron, the result is it deoxidizes the initial slag so much the heat melts higher in carbon than is wanted. Fig. 1 shows the course of carbon elimination for a given amount of pig iron in the charge; curve 1 for high-silicon iron, curve 2 for normal silicon iron, and curve 3 for low-silicon iron.

The first slag formed is usually fairly high in iron oxide because scrap has been oxidized all the time. If 1 per cent. silicon pig iron is charged for and 1.5 per cent. obtained, more has been deoxidized than expected, and there is not enough iron oxide to eliminate carbon. That will come down and the melt may be at 1 per cent. carbon.

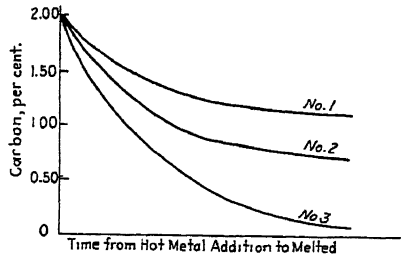


FIG. 1.

If low-silicon iron is obtained there is so much iron oxide the melt is soft and the carbon comes down as in curve 3, Fig. 1, and it is necessary to pig back. Most operators believe it is better to melt as in curve 2 and use a small amount of ore than to melt low and pig back, although one plant in particular makes a practice of melting soft and pigging back. They are using a large amount of hot metal and cannot use it at one time in the furnace.

One disadvantage of low-silicon or high-silicon iron is that either the melt is too high or too low. Furthermore, to get 1.60 or 1.65 per cent. silicon pig iron when trying to make 1 per cent. would indicate that the blast furnace was not giving the kind of iron wanted. That is a point to be discussed later on. We found that with irregular blast-furnace operation more oxides were obtained in the steel all the way through than with the blast-furnace operation uniform. So a high-silicon or low-silicon iron would indicate that the pig iron was not all of the quality desired.

The other important point is that the melt is too high or too low and the furnaces are not kept on schedule. Another disadvantage of low-silicon iron is the heavy slags. With high-silicon iron the banks are cut a great deal and excess lime must be put in as you go down the heat.

C. L. KINNEY, South Chicago, Ill.—Within the higher ranges of silicon the slag volume is increased enormously, which is an added economic disadvantage in terms of metallic loss and added fuel and slag handling costs.

C. D. KING.—Does the question of run-off slags qualify the reference Dr. Herty makes to the use of high or low silicon, the last statement regarding the disadvantage or advantage of high and low-silicon pig iron and the low or high melts?

C. H. HERTY, JR.—With a run-off slag, one is usually in the position where ore has been charged in the first of the heat in order to get a flush. There would be a larger percentage of pig iron in the charge and the effects would not be felt as much as if there had not been any ore charge. There is a little factor of safety effective there. Balance is effected by using a flush slag. The silicon in the iron has a considerable effect on the kind of flush slag, the amount, and when obtained.

CAUSES AND CORRECTION OF FOAMING

C. D. KING.—Another phase of the silicon question relates to the foaming of heats. What causes heats to foam and why do heats foam more with natural gas than with oil or producer gas? How can this foamy condition be corrected?

C. H. HERTY, JR.—T. T. Read, at the Open-hearth Conference at Youngstown (May 3–4, 1928) explained what made heats foam, in terms of beer and ginger ale. Beer has high viscosity and ginger ale has not, so beer foams more.

A heat foams because gas is given off on account of carbon elimination and the gas cannot get out of the slag. That makes a slag rise high in the furnace and causes foam. Two things will give a foamy slag for a given type of fuel—carbon coming off so fast that the slag will not release the gas rapidly, and a slag condition that will not allow more than a certain amount of gas to get out at a time. I believe that for a given type of fuel there is a range of slag composition with a surface tension which makes heats foam. Combine surface tension with temperature and I think you have the answer. The only difficulty is that we do not do anything about surface tension in slags. Until we do we can hardly tell how to correct the foaming.

Foaminess can be corrected by adding lime or silica. We have had experience with very high-lime slags and silica sand. Upon addition foaming ceased almost immediately and carbon elimination continued at normal rate.

On the sixth page of my paper, I said that "unfortunately, so far as the writer is aware, few operators take the trouble to take slag samples during foamy periods," and already three or four operators have begun to take them. Possibly we will have some answer to that particular problem as we get some analyses.

With the different fuels, it depends on the weight of the gas as to how it will hold the foam down. The foam can be held down fairly well with tar or oil because there is a heavy stream beating on the slag. If natural gas is used the stream is much lighter. There is more foaming with natural gas and coke-oven gas than with tar or oil, and producer gas would, I believe, be between the two.

As far as foaming is concerned, the primary condition is slag viscosity and surface tension and the speed of gas elimination. Not enough gas is given off with the high-silicon iron to make the slag foam. If the carbon dropped very fast an extra amount of gas came off. With a very foamy slag, heat transfer from slag to metal is cut considerably and temperature is lost.

F. B. MCKUNE, Hamilton, Ont.—The worst foaming we have is on the low-silicon iron. This foaming starts before we begin to get up any of the lime; as soon as the lime starts up, the heat will settle right down.

C. H. HERTY, JR.—Fig. 2 of my paper shows a composition-viscosity curve for lime-silica slags on which may be noted a range where high viscosities are obtained with two different compositions of lime and silica. I think that with a lime-silica ratio as shown on the left, and added lime, that condition would be eliminated. With the lime-silica ratio on the right, silica could be added successfully. This is a viscosity curve simply for lime-silica slags. What it would be with manganese and iron oxide, I do not know. As one goes to the high-lime side there is likely to be more foam, and that is about what the analyses are showing—35 or 36 lime and 28 silica, instead of lower limes. We are continuing work on viscosities of these slags.

R. SIMMONS, Monessen, Pa.—We usually get foaming whenever the hot metal is delayed, and when Mr. Kitto received Dr. Herty's paper, he immediately went out and found two heats where the hot metal was delayed and took the analyses of those slags.

The first heat was a so-called ore heat; the charge consisted of 60 per cent. hot metal and 40 per cent. scrap, with 21,000 lb. of manganate ore on the lime. The lime burden was 22,400 lb. The total metallic weight of the charge was 215,200 lb. This heat required 6000 lb. of hard ore and no fluorspar to bring to a tapping point of 0.10 per cent. carbon. It required 4 hr, to charge the scrap burden on this heat, and hot metal was not added until 50 min. after the scrap was all in the furnace. The

first slag was flushed off the furnace 10 min. after the hot metal was charged. The flushing was finished in 45 min. The slag sample was taken 15 min. after the flushing period, while the heat was foaming badly. The analysis of this slag sample is as follows:

	Per Cent.		Per Cent.
Silica	20.80	Lime	33.00
Iron	14.50	Magnesia	6.30
Manganese	9.80	Sulfur	0.114
Phosphorus	1.96	FeO	15.45
Alumina	2.80	Fe_2O_3	2.40

The second heat was a so-called scrap charge. It consisted of 53 per cent. scrap, 13 per cent. cold pig iron, and 34 per cent. hot metal. The lime burden was 28,600 lb. The total metallic charge was 216,600 lb. This heat required 5000 lb. of hard ore and 150 lb. of fluorspar to bring it to a tapping carbon of 0.20 per cent. It required 1 hr., 40 min. to charge the scrap and cold iron burden, and the hot metal was not added until 4½ hr. after the cold charge was all in the furnace. The heat began to foam actively immediately on charge of hot metal, and the slag sample was taken 10 min. after the hot metal addition. This sample analyzed as follows:

	Per Cent.		Per Cent.
Silica	21.94	Lime	31.00
Iron	15.30	Magnesia	3.31
Manganese	13.80	Sulfur	0.122
Phosphorus	1.46	FeO	17.88
Alumina	1.56	Fe_2O_3	2.00

The hot metal going in both these heats could not be considered of low silicon content. The analysis was as follows: silicon, 1.22 per cent.; sulfur, 0.034; phosphorus, 0.270; manganese, 2.04.

In my opinion, high silicon in the charge is more likely to accompany these foaming slags than low silicon.

C. H. Herty, Jr.—I think you will find that with the higher silicon iron during this particular period the average slag will run 35 silica and 30 lime on the heats that do not foam. I have a number of analyses on heats that do not foam and usually silica and lime are about 1 to 1 during the same period that Mr. Simmons spoke about. If there is this kind of slag with low-silicon iron, there is foaming, particularly if the hot metal is delayed, which means that carbon will begin to eliminate rapidly.

F. B. McKune.—I wonder what effect dolomite would have. The heat I have in mind would take about 8000 or 10,000 lb. of dolomite and we find the bottoms score very badly.

C. H. Herty, Jr.—I should think that as the magnesia was increased the slags would cause the heats to foam more. The magnesia would probably tend to thicken the slag. If there is a foamy slag on one heat eliminating carbon at the rate of one point per minute, and another at two per minute, there is a much better chance of getting a foamy heat on the second, where carbon is eliminated twice as fast, because more gas is being forced out.

F. B. McKune.—We find these heats melt very close. As a rule they melt soft.

C. H. Herty, Jr.—That would indicate fast carbon elimination.

F. B. McKune.—It carries out your idea of eliminating carbon before you get the heat shaped up.

C. H. HERTY, JR.—If, because of foamy slag, the gas is directed toward the roof, the furnace roof and back walls are damaged, and the foaminess of the slag increases the time of the heat considerably. A very foamy heat takes longer to work than one that is not foamy.

H. D. HIBBARD.—Foam and boil are not the same thing. The foamy slags I have seen generally were accompanied by a rather slow oxidation of carbon. Rapid oxidation of carbon does not cause it.

C. H. HERTY, JR.—There can be slow or fast carbon elimination—two different kinds of carbon elimination and slag, but the same kind of foam.

C. L. KINNEY.—What effect has the physical condition of the ore upon the foaming condition, contrasting if you choose, lump or low-moisture ore with fine or high-moisture ore?

C. H. HERTY, JR.—I think the fine ores would produce much more foam than heavy ores, because more gas is given off.

C. L. KINNEY.—In the old wash metal process the oxidation was by means of a sintered ore bottom and a very slow reaction.

C. H. HERTY, JR.—With a very shallow bath you can get the ore quickly. The situation is different with a deep bath because the ore is worked out before it comes to the surface.

J. ALEXANDER, New York, N. Y.—I had occasion to make an investigation which I think throws some light on this, although it involved the frying of potatoes in fat. Certain fats, when used in frying potatoes, froth so that they boil out of the pan into the fire; in other fats, potatoes fry quietly because the gas bubbles which contain steam from the frying potatoes form and burst.

When frying potatoes at a rate of emission of steam, corresponding to the velocity of the emission of gas from metal, the fat will go over into the fire if the bubbles form more rapidly than they burst. It is a question of relative velocity of formation and bursting.

If a fat is used which makes a bubble skin so viscous that it will not burst rapidly enough, of course the bubbles begin to accumulate, rise into a froth, and the fat boils over. You will find on close observation[1] that when a bubble forms there is a tendency for it to become thin at the top, because the wall of the bubble flows down under the action of gravity. Then the viscosity factor comes into play.

A great many principles can be illustrated by experiment on a kitchen stove. If one keeps within a certain viscosity limit and elimination of gas is not too rapid, he will not get out of the frying pan into the fire.

EFFECT OF HIGH MANGANESE ON SULFUR CONTENT

C. D. KING.—The next question deals with manganese and sulfur. I would prefer to group these to make one question and let Dr. Herty answer the whole phase. What effect has high manganese on the sulfur content of pig iron and on the fluidity of the slag in the open-hearth operation as well as on the elimination of silicate impurities?

C. H. HERTY, JR.—I will take up first the effect of high manganese on sulfur in pig iron. I think it is generally true, although I must confess I do not know why,

[1] R. E. Wilson: Surface Films as Plastic Solids. Colloid Chemistry, Ed. by J. Alexander, 1, 276. New York, 1926. Chemical Catalog Co.

that the high-manganese irons tend to be lower in sulfur at the blast furnace than the low-manganese irons. Secondly, there is the solubility of manganese sulfide in iron to account for.

We have done some work on the solubility of MnS in iron under certain set conditions in the laboratory. This does not apply directly to a blast-furnace ladle, but we can talk about solubility in these terms. If the manganese and sulfur are ionized in the melt, the concentration of manganese times sulfur should be constant for a given temperature. This is expressed as $(Mn)(S) = K$. With 2 per cent. manganese and 0.035 per cent. sulfur at equilibrium, $K = (2.00)(0.035) = 0.070$. As the manganese content is lowered or raised the sulfur will increase or decrease according to the relationship $(Mn)(S) = 0.070$.

As the temperature increases, the manganese sulfide solubility increases rapidly. At the temperatures obtained in a blast-furnace ladle—2400° F. at the point of destination of the ladle—K is equal to about 0.07. If the temperature is increased to 2500° F., K becomes 0.10. At 2900° F., which is an average temperature for steel, K becomes 0.80.

The amount of sulfur that must be eliminated from pig iron can be determined from the values of K, provided the temperature drop occurs from blast furnace to point of destination and the manganese sulfide is given time to get out of the metal, and also provided the iron is fluid enough for the particles to rise.

For normal operation at 2400° F. in the mixer the value of K should be about 0.070, and at 2500° about 0.10, so that if you had 2 per cent. manganese iron you would expect a drop to 0.035 and 0.050 per cent. sulfur at the mixer for these two temperatures. This has been checked up very closely at two plants.

As far as steel is concerned, the value of K is so high at steelmaking temperatures that there is no elimination of sulfur upon the addition of manganese. In making a 1.40 manganese steel, sulfur is not dropped from the furnace test to the finishing test, because the solubility of manganese sulfide is so high elimination does not occur. The only possible way to effect elimination is to get the metal cold enough toward the end of pouring so that the solubility of the manganese sulfide is exceeded. That is counterbalanced by the oxidation of the slag and pick-up from the ladle, which tend to throw sulfur back into the metal.

That is the effect of manganese on sulfur elimination. A high-sulfur iron can be used at the blast furnace if the manganese is high and it is treated properly. I know of one plant that carries about 2 per cent. manganese iron. They often run into 0.050 and 0.060 per cent. sulfur. They eliminate the sulfur; by the time it gets to the open hearth it is down to 0.035 per cent. Then they dump the ladles upside down and pour all the manganese sulfide to the open-hearth furnace. On the other hand, if the iron is skimmed properly at the mixer and the open hearth, a considerable drop in sulfur may be obtained by utilizing the manganese.

There are two distinct effects of manganese in the open hearth; (1) increased fluidity of the open-hearth slag helps in working the heat; (2) high MnO in the steel helps to flux out any oxides present in the bath, and greater elimination of oxides with higher residual manganese results. Higher residual manganese means a little saving in ferromanganese. More important, however, is the presence of sufficient manganese in the steel to help flux out some of the impurities. That is particularly helpful in high-carbon steels.

R. W. H. ATCHERSON, Gary, Ind.—It has not been our experience that high manganese lowers the sulfur in the iron. We operate probably one-third of our blast furnaces on low-manganese iron for duplexing, and the remainder on high-manganese iron for basic practice. We do not feel that the sulfur is any lower on the high-manganese iron.

C. D. KING.—Bearing out what Dr. Herty says about skimming at the mixer and the sulfur content, I want to refer to three analyses which may contain some blast-furnace slag—they are 0.32, 0.79 and 1.26 per cent. sulfur.

W. E. BUCK, Granite City, Ill.—Our blast furnace is about 2 miles from the open hearth and the metal is transferred in Treadwell enclosed-type ladles. When the metal comes over from the blast furnace and the blast-furnace report shows a fairly high sulfur, we find a considerable drop in the samples taken from the ladles that go to the open hearth, especially if the metal has stood for some time after tapping from the blast furnace. The metal is transported in full ladle cars and apportioned out as needed at the plant. The remainder is sent back to the casting machine and quite frequently, more so in the past than in the present practice at the blast furnaces, there is a drop of as much as 0.015 per cent. in the sulfur content between the blast-furnace and open-hearth samples. It is probably due to the cooling of the metal and the separated-out manganese sulfide floating to the top. Of course, the Treadwell ladle has a small pourout and skimming is comparatively easy.

A. L. FEILD.—One question that occurs to me has to do with the loss of sulfur from pig iron in transporting the latter from the blast furnace to the open hearth. Does the manganese sulfide separate entirely as a result of decreased solubility due to temperature drop or does diffusion across the slag-metal interface also account to an appreciable degree for the observed drop in sulfur?

C. H. HERTY, JR.—The only observation I have is as reported by Mr. Buck. The ladles must stand some time to get the proper results. Unless they stand at least 40 min. there is not much desulfurization. The longer they stand up to a certain point, the more sulfur goes off. Apparently, after all the sulfur has floated out the metal is cooling so slowly there is not much drop in solubility. I believe the sulfur would come out all through the metal; primarily, of course, at the sides and top where it is cooling most rapidly.

C. D. KING.—This is probably one of the most important parts of this discussion. I think we should cover it thoroughly before going on.

G. B. WATERHOUSE.—One of the commonest ways of trying to get sulfur out of a heat when the heat is fairly well toward the end is to work through a box of spiegel. That is practiced in a great many plants. Dr. Herty does not seem to think it is going to work well. His temperature is high, constant around 0.8 as he calls it. He evidently thinks the lapse of time is going to help.

C. H. HERTY, JR.—We are talking about steel now. I said that if you put spiegel or pig iron, in a heat, the important point is simply to get the slag in shape and agitate sufficiently to scrub out the sulfur. If the slag has not been in good shape up to the time the spiegel is added, not much absorption of sulfur has been accomplished. You must have CaO and bring FeS into contact with it. Spiegel and pig iron usually give enough action to dissolve the lime if there is a raw heat and enough agitation to bring sulfur up to the surface to be scrubbed. I think that is the action there. I have plenty of figures on spiegel where there is no drop in sulfur because the sulfur is already low.

J. T. MACKENZIE, Birmingham, Ala.—Apropos of sulfur elimination, I have recently gone through a series of cupola melts that might be interesting. I melted in a cupola some white iron with 0.75 per cent. sulfur and about 0.10 per cent. manganese. I melted it three times without slag or additions and obtained no sulfur reduction whatsoever. I then proceeded to add 1 per cent. ferromanganese and some silicon in another series of melts.

On the first melt the sulfur came from 0.75 to 0.44. On a second melt on the same metal the sulfur dropped from 0.44 to 0.39, with the same manganese addition. The manganese in that case came out at 0.40, showing a loss of 0.65 per cent. manganese for that melt. The normal loss in manganese for low-sulfur metal would be in the order of only 0.20 per cent.

On another melt a ladle was tapped at 1468° C. and a set of bars poured at 1392° C. The ladle was held in a gentle rocking motion until the temperature reached 1289, when another set was poured. The analysis showed:

	First Set	Second Set
Pouring Temperature	1392	1289
Sulfur	0.189	0.147
Manganese	0.58	0.48
Loss of sulfur		0.042
Loss of manganese		0.10

It is my opinion that in these melts the fluidity of the metal is of primary importance; but certainly the manganese causes a very great tendency for the sulfur to come out. My opinion is that if the slag is of such nature that it will take the manganese sulfide, as it rises, away from the field, the desulfurization will be very rapid in the presence of manganese; but if the slag is inactive the manganese will simply run backward and forward between the slag and metal.

G. E. Thackray, Bethlehem, Pa.—What would be the reaction in such a case if a mixer is used instead of a ladle?

C. H. Herty, Jr.—In bringing the iron to the mixer there is a drop in sulfur which will depend appreciably on the temperature in the mixer. If the mixer is very cold there is likely to be considerable elimination of sulfur, and if it is hot, there will be practically no elimination of sulfur. Elimination is controlled by the temperature and to some extent by mixer slag composition. Williams[2] showed that as the ratio of silica to manganese in the mixer slag increased, the amount of desulfurization decreased considerably.

C. D. King.—The next phase of the discussion deals with slags, concerning which the least is known. In what form does iron oxide exist in slag? That is the first question.

Form of Iron Oxide in Slag

C. H. Herty, Jr.—On this question I should like to get the opinion of Professor McCaughey and others who have been working along these lines. What we usually consider in a basic furnace is the FeO in the slag. In the solution in the slag the Fe_2O_3 is usually combined with lime. Obviously, we know fairly well that the oxidation of the slag is carried out at the slag gas-surface, FeO oxidizing to Fe_2O_3, this being carried down to the slag-metal surface and reduced by iron, FeO plus oxygen or CO_2, giving Fe_2O_3, and that being carried down to the metal surface and oxidizing the iron to give FeO.

We found that the solubility of iron oxide in pure iron under a basic slag—that is, under a slag containing no acids—is just the same as if there were pure iron oxide in equal concentration in the slag.

In a slag containing 50 per cent. iron oxide and 50 per cent. lime the FeO acts as though it were all in solution in the slag. With acid slags there is less oxygen in the metal than under basic slags, which shows that some of the iron oxide is combined with

[2] S. V. Williams: Control of Sulphur in the Basic Open Hearth Process. *Blast Furnace and Steel Plant* (1923) **11**, 51.

silica. This is particularly true of flush slags with 15 per cent. lime, 25 per cent. silica, 20 to 30 per cent. iron oxide, and 10 to 15 per cent. manganese oxide. If the iron is combined as iron silicate, the metal does not oxidize as rapidly as it does when the lime is higher and the silica lower. I believe it is nearly all in solution in the basic slag. That is why the basic furnace works as fast as it does.

W. J. McCaughey, Columbus, Ohio.—Our study of open-hearth slags has been from the viewpoint of mineralogical composition—that is, to determine the compounds which are formed by the oxides comprising the slags. We identify these compounds by determining their optical properties with a petrographic microscope, using also X-rays for further indentification.

We are not able as yet to interpret the properties of a slag in terms of its mineral composition. In regard to the number of compounds or minerals present, an open-hearth slag is simple—there are ordinarily two or three compounds present. One of these is a silicate, the other is a compound oxide containing no silica. The silicate mineral is probably a calcium silicate of the orthosilicate type but its optical properties are somewhat different from the pure compounds described in the researches of the Geophysical Laboratories.

Iron oxide of the finishing slag is found principally in the oxide mineral, not in the silicates. Lime is a much more active base than is FeO or MgO, and free CaO in a slag would be effective in forcing MgO and FeO out of combination in silicates.

When iron oxide is in the form of ferric oxide, it unites readily with one or two molecules of CaO to form easily fusible compounds known as ferrites. Under reducing conditions FeO does not react readily with CaO and does not form readily fusible compounds.

Magnesium oxide, unlike CaO, does not form fusible compounds by reacting with Fe_2O_3 even when the latter is in large excess. Magnesioferrite, ($MgO.\ Fe_2O_3$) contains only 20 per cent. MgO and 80 per cent. Fe_2O_3, yet this compound is a refractory. There is then a striking difference in the reaction of CaO and MgO with Fe_2O_3, forming in one case a very fusible compound, in the other case a refractory compound. These ferrites also show considerable difference in reducing reactions. The calcium ferrites are fairly easily reduced, yeilding the two oxides CaO and Fe_3O_4 and later even metallic iron.

Magnesium oxide as periclase takes up in solid solution 40 per cent. Fe_2O_3 (determined by X-ray analysis). In this state and as magnesioferrite the compounds resist reduction—the magnesiun oxide tending to preserve the iron oxide in the form of the sesquioxide.

Manganese oxide is occasionally found as such in slags but is generally found in solid solution in calcium oxide. We have found MnO (as manganosite) as a nonmetallic inclusion in steel, identification made by its optical properties under a petrographic microscope and also by X-ray analysis. Calcium oxide and manganese oxide react readily with one another to form an almost complete series of solid solutions. From the researches of the Geophysical Laboratory, no solid solution exists between CaO and MgO.

It is difficult to get CaO to take up FeO in solid solution, possibly because of the difficulty of keeping the FeO as such, but in the presence of MnO there is a ready solid solubility of both FeO and MnO in CaO. Apparently there is a wide range in composition of these solid solutions.

In the early slags of the open hearth, the iron oxide is found in the silicate mineral but as the lime comes up it displaces the iron oxide and manganese oxide from the silicate, these separated oxides forming with CaO, the oxide mineral, which gradually increases in amount. The oxide mineral or solid solution of CaO.FeO.MnO and possibly other substances is easily susceptible to oxidation and reduction reactions and

it is believed that the refining properties of the slag are closely related to this oxide mineral.

In the silicate mineral present in the open-hearth slag we notice a continuous change in the optical properties of the silicate formed in the earlier part of the heat, as the heat progresses, indicating a change in its composition due to the reaction with CaO. After a time a new and different silicate appears. Fortunatley there is an abrupt change in optical properties and since one silicate is optically positive, the other negative, it is easy to distinguish them even in thin section. As the refining progresses the early silicate diminishes in amount; the later silicate increases in amount until the heat is finished. Long before the end of the heat the early silicate has completely disappeared.

We have not as yet separated these minerals from one another for separate analysis, so are not able to give their composition. The silicates are generally colorless and transparent in thin section. Their optical properties or the X-ray patterns do not agree entirely with the silicates of calcium worked out from pure materials by the research workers of the Geophysical Laboratory.

In several slags we have identified a mineral which agrees fairly closely in optical properties with the tricalcium silicate as found in commercial portland cement. The compound sometimes shows a pale green color in powder under the microscope—there is also a close agreement for four lines in the X-ray patterns. It is planned to separate these minerals from the other minerals in slags, to analyze them and submit them to X-ray analysis.

Apparently the tendency in mineral formation in finishing slags is to form silicates of calcium and to form an oxide mineral which is a solid solution of CaO, FeO and MnO and varies considerably in composition. Magnesia must function in a very limited way, since practically all slags contain but 4 or 5 per cent. magnesium oxide, and in the slags we often find the periclase (colored heavily with iron) as a separate constituent, probably as part of the bottom refractory.

Manganese oxide (manganosite) may be present as such but ordinarily it is present in solid solution with FeO and CaO, with which it seems to form almost a complete series of solid solutions.

Mr. Cape and myself hope to be able to give a report of the results of our investigation of the mineralogical composition of open-hearth slags at the February meeting of the A. I. M. E.

R. B. Sosman, Kearny, N. J.—We should be clear as to what we mean in speaking of "solubility" and "solution." Dr. Herty used the term "solution" several times as if in contradistinction to "combination." I understand him to mean "contained in a homogeneous phase, but not in chemical combination with silica." The expression might be misunderstood to infer a two-phase slag, a condition that probably does not prevail in the open hearth. The distinction Dr. Herty is trying to make, as I gather, is the distinction between the combination of the oxides into a homogeneous liquid silicate on the one hand, and on the other hand, the existence of this same homogeneous liquid, still as homogeneous as a glass of water, but with the oxide chemically free. We can make this logical distinction, but whether any externally measurable properties correspond with it in all cases is a problem that the physical chemist has not solved.

C. H. Herty, Jr.—That is a point I should like to bring out. Sometimes we do get immiscibility in open-hearth slags. I have seen two definite layers of slags on an open-hearth bath. Why it is, I do not know. There will be a slag with a very thin layer of secondary slag underneath. I have seen slags taken out of the open hearth that had two layers. Whether that has something to do with the particular stage of the heat, I do not know.

R. B. SOSMAN.—That is true in a number of silicate systems; lime, magnesia, ferrous oxide, zinc oxide, manganese oxide, all show liquid immiscibility. That is, near the silica side of the diagram there are two liquid layers which do not mix any more than oil and water will mix. A better comparison is phenol and water, where on one side there is a solution consisting of phenol containing a little water, and on the other side a solution consisting of water containing a little phenol.

W. J. MCCAUGHEY.—The use of bone phosphate in porcelains has been under investigation in the Ceramic Engineering Department of the Ohio State University. I have examined microscopically some frits or melts that have been made in this investigation and some of these give clear evidence of the presence of immiscible liquids. Whether or not some of these examples are the result of immaturity and slow diffusion or whether they are true examples of immiscibility will be brought out by the further investigations of Paul Collins under Professor Watts. Mr. Collins' work shows particularly clear evidence of immiscibility in orthoclase-bone phosphate fusions where the phosphate amounts to 40 per cent. Upon superheating this immiscibility is destroyed and a single liquid obtained.

HIGH IRON OXIDE IN SLAG

C. D. KING.—How can a high iron oxide in a slag be reduced and what effect has high or low iron oxide on the quality of rimming steels or on killed steels?

C. H. HERTY, JR.—Regarding iron oxide in the open-hearth slag there is simply a balance between what was put in and what is taken out. The iron oxide originates in a number of ways: (1) rust on the scrap—scrap rust; (2) oxidation of scrap during melting before scrap gets under the cover; (3) oxide in any ore put into the furnace as charged or during the working period; (4) decomposition of the calcium carbonate ($CaCO_3$) giving the lime boil, and CO_2 reacting with iron to form FeO. I have estimated that the reaction $CO_2 + Fe = FeO + CO$ is from 35 to 50 per cent. completed in the open hearth. I think Mr. King said he thought it was around 30 per cent. That is merely an estimate. So we have iron oxide from the limestone decomposition. That has a very definite effect in open-hearth work. A fifth way of putting iron oxide into the steel is the oxidation of the slag.

The way to take iron oxide out of the steel is by the elimination of the metalloids, carbon, manganese, phosphorus, and silicon. Whether a high or low iron oxide slag is obtained depends primarily on how much is put in through these five sources, and how much is taken out, and also how fast it is put in and taken out. At the same time there is a question of the total amount and rate.

Let us suppose we have a definite kind of scrap, a definite amount of oxidation, a definite amount of ore added and a definite amount of iron oxide from the limestone, and have a furnace atmosphere in two heats, one of which oxidizes the slag rapidly, and another slowly. If we can vary the fluidity of the slag and get the same rate of carbon elimination we would expect to find more iron oxide on the finishing slag on the furnace with the sharp flame than with the reducing flame.

That condition is difficult to simulate in practice because it is difficult to get two rates of carbon elimination under two such widely differing conditions. However, the iron oxide in the finishing slag depends on the difference between the input and the output, and the percentage depends on the difference between the two divided by the slag weight. Naturally, if the slag volume is increased the percentage of iron oxide decreases.

With a low-silicon iron one would expect a high percentage of iron oxide in the slag and vice versa. The reason for this relationship is simply that high-silica slag means a large slag volume and low percentage of iron oxide by dilution. That is one factor that

controls the amount of iron oxide, and the slag volume is controlled to a certain extent by the amount of silicon put into the furnace.

The amount and percentage of iron oxide depend on putting in the five items named, taking out iron oxide, and the speed of doing both. There are three ways by which the percentage of iron oxide can be reduced in open-hearth slag: (1) take the slag off and throw it away and put on a fresh one that is not oxidizing; (2) increase the slag volume, which nobody wants to do; (3) eliminate the metalloids at a faster rate than the rate of oxidation by the gas.

As the carbon content decreases, the rate of oxidation of carbon slows down, and the rate of oxidation of the slag usually picks up because the furnace is getting hotter. To control iron oxide in slag it is necessary to know how much is put in in various forms and how much it is expected to eliminate, and control ore additions accordingly. Control cannot be effected unless the slag is analyzed before an ore addition is made. Two heats melted at 0.80 per cent. carbon might each, on the carbon test, give the same amount of ore. One might have a good deal more iron oxide in the slag than the other. In order to control the iron oxide in the slag it is necessary to know what iron oxide is present before adding ore, and the only other requisite is to get as small oxidation of scrap as possible.

I wish I could answer the question as to the effect of iron oxide on the quality of steel. What is a rimming steel? Let us consider that in the first place. Let us say rimming steel is the type of steel where undeoxidized or incompletely deoxidized steel is poured into a mold so that a thick-skinned ingot is obtained, and where enough gas is given off to prevent gas holes in the ingot.

MEMBER.—I would consider rimming steel an incompletely killed steel which on freezing evolves gases. This evolution is known as rimming and is a practice adopted to obtain a sound skin only. Rimming steel has many inherent defects, but usually it is used with a full knowledge thereof, as, for instance, in the manufacture of seamless tubes, where fairly sound center and skin are necessary.

C. H. HERTY, JR.—In order to get the sound skin and as good a condition in the center as possible, there must be a proper evolution of gas in the mold, and I think that is where the iron oxide in the slag is effective. If there is too much iron oxide in the slag in the furnace and the action in the furnace is too violent, too much gas is given off in the ingot. Usually the consequence is a very thin skin and many blowholes. With a slag too low in iron oxide there is not sufficient action to sweep the gas away as formed. The gases are trapped if the current is not brisk enough to carry them out.

That is what Mr. Hibbard meant in his lecture on the Significance of the Simple Steel Analysis.[3] If the action in the ladle is too violent one can guess at the desirability of killing that action in the mold by adding aluminum or some other deoxidizer in addition to the manganese to cut down the gas evolution. If the evolution of gas in the furnace is too small—and that means too small an evolution of gas in the mold—there is nothing that can be done other than to take the poor rimmed ingot, which will rise in the mold.

There are two limits, controlled primarily, I think, by the iron oxide of the slag. It is open to discussion of other factors than the iron oxide in the slag. I believe the high-oxide slag gives too much and the low too little gas evolution, both of which are bad. There is a desirable optimum of gas evolution. That is the important feature of making rimmed steel—getting the proper rate of carbon elimination at the end of the heat.

---

[3] H. D. Hibbard: Significance of the Simple Steel Analysis. Howe Memorial Lecture, 1928. *Iron and Steel Technology in* 1928, A. I. M. E., 7.

Just how that can be controlled other than by the iron oxide in the slag will be developed in the discussion on rate of carbon elimination. In killed steels it is important to get as low iron oxide as possible and still have proper action in the furnace to clean up the steel.

Control of Rate of Carbon Elimination

A. L. Feild.—In order to bring together these questions of iron oxide in the slag and of rate of carbon elimination, Mr. King propounds the question, how can the rate of carbon elimination be controlled? Dr. Herty has spoken on the control of iron oxide in the slag. It seems to me that carbon elimination control would follow obviously as the way, in part, of controlling rate of carbon drop.

C. H. Herty, Jr.—I admit that three months ago I could have answered that much better than now. We used to think that the elimination of carbon from steel was simply a question of the speed at which FeO was fed into the bath. The carbon and iron oxide were essentially at equilibrium at all times and the rate at which FeO was driven from the slag into the metal was governed by the iron oxide content of the metal and slag.

Suppose a heat is at a given carbon and has 0.02 per cent. oxygen present and a slag which would saturate the metal with 0.10 per cent. oxygen if there was not any carbon present. The iron oxide in the slag tends continually to give up 0.10 per cent. oxygen to the metal. The difference between the two oxygen contents, or 0.08 per cent., would be the driving force to form iron oxide in the metal, and that would control the rate of carbon elimination.

Under those conditions we have found that if the percentage of carbon is multiplied by the percentage of iron oxide in the steel a value of about 0.008 to 0.016 is obtained. If the carbon is known the iron oxide can be ascertained and one can say that 0.008 was the driving force which regulated the rate of carbon elimination.

Some recent work by Mr. Kinzel and Mr. Feild of the Union Carbide and Carbon Research Laboratories seems to indicate that instead of 0.012 and 0.016, the product is 0.0005. In the open hearth we get between 0.008 and 0.016 consistently. Actually at equilibrium one should get 0.0014. The oxygen is about 20 times higher than it should be.

The experimental work was very good, I think, and has been checked in a number of ways. There is some explanation of why steel made in the open-hearth furnace should contain 10 times as much oxygen as that called for by equilibrium. This condition is responsible to a certain extent for miscalculation of the rate of carbon elimination. The best way to ascertain the rate of carbon elimination is to stay around the furnace and get it oneself. What it is going to be is not known. It may be that certain things like inclusions in steel act as nuclei for the gas bubbles to form upon. If that happens they can probably be formed at low pressure so that much less oxygen would be released than indicated.

An absolutely clean steel, instead of taking 10 times the amount of oxygen, might take 15 or 20 times that to form the gas bubble and let it escape. I think this particular point is as startling from the standpoint of what goes on in the open hearth as anything I have learned since I first became interested in the open-hearth furnace.

We cannot say that if the steel contains a certain amount of carbon it will contain a certain amount of oxygen, because we know it will not. We get a variation which is much higher than we actually should have from equilibrium measurements. If we could find some way to make the oxygen come off at one atmosphere there would not be enough oxygen to worry about. The amount would be so small that it would pay to throw away all the apparatus for determining oxygen in steel and forget about it.

How we are going to do that is beyond me. One thing I am going to try is to kill a heat with aluminum, let it reboil and see if the very fine alumina particles have an effect.

I do not know why we should get from 0.008 to 0.016 instead of 0.0005. There is an explanation somewhere. If we can find that it will change steelmaking processes more than anything else.

A. L. FEILD.—This question of the equilibrium constant to which Dr. Herty refers is one to which both he and I have been giving a good deal of thought for several years. On the basis of his own work he arrived originally at a fairly high constant. More recently[4] he has arrived at a considerably smaller constant of 0.016. On the basis of theoretical considerations relative to rate of carbon drop and other operating factors, I concluded that 0.016 still remained on the high side. About a year ago I gave a value of 0.01, which was thought at that time by Dr. Herty and others to be too low.

Since my paper on this subject was presented to the Institute a year ago, the problem has been again approached, and from two directions. In the first place, it seemed exceedingly important to measure this equilibrium experimentally. The simplest method that suggests itself is that of observing the static equilibrium condition reached in an atmosphere of CO.

A. B. Kinzel, working at the Union Carbide & Carbon Research Laboratories in Long Island City, undertook and has carried through to successful completion this experimental program. He has found that under a CO pressure of 1 atmosphere, the product of carbon and FeO, expressed in per cent. by weight is equal to approximately 0.0005, which is 20 times as small a value for this constant as the lowest value (0.01) which had been suggested on the basis of open-hearth data.

When this decidedly unexpected result was obtained, I undertook to obtain substantiating evidence from a theoretical calculation involving chemical thermodynamics. Such a calculation had been attempted in the past by others and the results published, but there had been no way for these previous workers to tell whether their calculations were even approximately correct or not. The first attempt had been made by LeChatelier. Haakon Styri used the method of LeChatelier and arrived at a somewhat smaller calculated constant. Using more accurate data recently available, I have obtained a calculated value of 0.001 for the product of carbon and FeO under a CO pressure of 1 atmosphere. This value is only twice as large as the experimentally measured value of Mr. Kinzel, and, in view of the nature of the calculation, this is combined to represent as close an agreement as could be reasonably expected.

As Dr. Herty has said, if the equilibrium constant is as low as 0.0005, it should be possible to remove practically all the carbon from steel and at the same time leave in the steel an exceedingly small percentage of dissolved FeO.

PRESSURE OF CO IN STEEL

Dr. Herty has made the suggestion that the pressure of CO in the steel may be higher than we think it is. However that may be, what has been done at the Union Carbide & Carbon Research Laboratories represents a decided step, we feel, in the direction of getting exact data and shows the value of experimental work, conducted in a laboratory, in connection with practical steelmaking problems. Possibly Mr. Kinzel has a few words to say.

---

[4] C. H. Herty, Jr. et al.: The Physical Chemistry of Steel-making: Deoxidation with Silicon and the Formation of Ferrous Silicate Inclusions in Steel. U S Bur. Mines *Bull.* 36, Min. & Met. Investigations (1928) 60.

A. B. KINZEL, New York, N. Y.—The experimental results obtained at the laboratory, by Mr. Egan and myself, were so surprising that we withheld them from publication in order to check and cross-check them. We have already done sufficient work to feel quite sure that the value obtained is of the correct order of magnitude; that is, about 1×10^{-4}. The figure given is for 1550° C. We expect to present a paper before the Institute at the fall meeting describing in detail the experiments and the results.[5]

We have given considerable thought to the significance of the observed constant when applied to the open hearth. We believe that it may be reconciled with the figures apparently effective.

It is obvious that the assumption of a high CO pressure is one possibility. Another one is the actual rate of reaction. If the rate of reaction changes very rapidly with the temperature, it is conceivable that the rate of carbon drop should follow the curve that it does in the open hearth and the equilibrium constant still be what we find it to be.

It is necessary to use the imagination a little in order to visualize a change in quite that way, but at any rate it is another possibility. All we are doing is to shed some light on the phenomena. We are then speculating and hope everyone interested in this problem will give it his best thought to see if we cannot arrive at a better understanding of what really happens in the open hearth.

The matter of temperatures just mentioned is most important, and always seemed to be one of the unfortunate things about open hearth, particularly in practice, as usually no attempt is made to measure the temperature. We have a very rough idea of what it is.

Larsen, in his paper reviewing the subject of steel-temperature measurements, has gone into pyrometry quite thoroughly. I cannot add much to what he said. He has shown the serious errors which can be very readily introduced in the use of an optical pyrometer. Recently, I understand, thermocouples have been developed which it is hoped will be applicable. You have probably read one paper on this presented at the Electro-Chemical Society by the General Electric engineers.

In view of the extreme importance of temperature, particularly in actual furnace operation where it determines how long we can hold a heat and the best time to tap it as far as skull loss goes, I have done some work on its determination.

It occurred to me to go back to the old method of measuring temperatures; namely, calorimetry. Offhand that does not seem practicable for an open-hearth furnace. Of course it is tied up intimately with the materials used.

In discussing Mr. Feild's paper a year ago, I mentioned the possibility of introducing a ball of a known weight in a container that will stand both the steel and slag, putting the ball in a calorimeter with either no loss or standard loss, calibrating beforehand, of course, and thus getting a fair measure of open-hearth temperatures. Since that time we have constructed an apparatus somewhat on that order, not with any idea of actually getting open-hearth temperature, but finding out whether the idea had any merit.

Through the courtesy of Mr. Meissner of the Chrome Steel Works, we took the apparatus to his melting floor and tried it out on one of their furnaces. It consists simply of a graphite tube on a suitable holder with a small graphite ball placed in the bottom of the tube. The tube is immersed in the liquid bath. We found it was necessary with the tube we were using to hold it in the bath no more than 40 sec. in order to get consistent readings. In taking out the graphite tube it is at metal temperature and may or may not be covered with some slag, but regardless of the condition it seems that the time between taking it out of the furnace and dropping the ball in

[5] A. B. Kinzel and J. J. Egan: Experimental Determination of Equilibrium in the System Iron Oxide-carbon in Molten Iron. See page 304.

the calorimeter is short enough so that the ball temperature is unaffected. The latter is no mean task, by the way. The temperature rise is constant on readings taken a few minutes apart in the open-hearth furnace. That is essential, because if they are we can go back and calibrate.

If anyone is interested in going into this further, the Union Carbide & Carbon Research Laboratories staff would be very glad to cooperate. We ourselves are not steel producers, as you know. We have the temperature problem partly solved. Certain mechanical details have to be worked out. We feel we have shown that the system has merit and is worthy of further consideration.

A. L. FEILD.—Dr. Alexander has asked about the general nature of the method of measurement which was used in determining the equilibrium constant.

A. B. KINZEL.—It consists of holding molten iron or steel with oxygen and carbon content known before the test in one atmosphere pressure of CO, said pressure controllable and at an accurately measured temperature controllable by means of an electric furnace. The whole thing is carried out in a furnace originally meant to be a vacuum furnace and the melt held a sufficient length of time for equilibrium to be established, varying the time factor until we know that equilibrium does exist. The furnace is arranged with cooling coils so that we can get rapid cooling from temperature and thus fix our conditions at that temperature. The ingot is then analyzed for oxygen and carbon. This is done starting with materials free from the usual impurities, silicon, manganese, sulfur, phosphorus, and so on, but with varying initial oxygen and carbon contents.

We have introduced carbon near the system to be sure the CO is in equilibrium with carbon, but this made no difference. In fact, we have gone through a number of variations but always wind up with the same figure, even though the results are so far from what we expected.

J. ALEXANDER.—Any slag?

A. B. KINZEL.—None.

J. ALEXANDER.—One of the advantages of having a foam in beer is that the foam can keep in the carbon dioxide. Might not that be the situation here where the slag layer will tend to keep the carbon monoxide in the metal?

A. B. KINZEL.—As I see it, the analogy is imperfect. Carbon monoxide in the open hearth comes up into the slag, either reacts there or goes right on through. We are not dealing with a foamy slag.

J. ALEXANDER.—You have a layer.

A. B. KINZEL.—But not one high in CO content.

J. ALEXANDER.—Does it not exert some opposition to the passage out of the CO?

A. B. KINZEL.—Yes, certainly, but hardly enough to account for the phenomena in question.

A. L. FEILD.—I believe the pressure would have to be 10 to 20 atmospheres. Before Dr. Herty comments on this—and I know he has something interesting to say—I wish to call attention to an interesting point observed in making these melts in an atmosphere of CO. Something was discovered which we could have predicted beforehand; namely, that if the volume of CO is large in comparison with the weight of the melt, the observed equilibrium is of the invariant type. The same is true when CO is continuously passed over the molten iron. The system involved is made up of

three components in two phases with a maximum number of degrees of freedom of three. But in the present experimental procedure, (1) temperature, (2) pressure and (3) composition of the gas phase are fixed; hence the composition of the liquid phase is likewise fixed and the system is invariant. At equilibrium, not only is the product of carbon times FeO constant, but the carbon percentage was the same and the FeO percentages were each individually constant for a given temperature and pressure of CO. It might be added here that for a given temperature the equilibrium percentage of FeO is independent of the CO pressure whereas the equilibrium percentage of carbon is proportional to the square of the CO pressure.

C. H. HERTY, JR.—About these temperature measurements: In connection with work of the U. S. Bureau of Standards in Philadelphia on measuring temperatures, we got, by the use of a couple in a special refractory tube, a temperature of 1685° C. and the optical reading on the end of another tube inserted without any couple gave 1687° C.—only 2° difference.

Mr. Gaines was the originator of the idea of high CO pressure. He will discuss that phase of the subject.

J. M. GAINES, JR., Pittsburgh, Pa.—I think that the open hearth and the evolution of CO are analogous to a dish of water on a stove. The CO pressure tends to build up until it becomes enough to form a bubble and the same thing is true of water heated upon a stove. It is a well-known fact that liquids can be superheated above their boiling points because the pressure exerted by the tension of the liquid on a small bubble becomes larger as the radius of the bubble becomes smaller. As the bubble starts from nothing, it obviously has theoretically to develop infinite pressure in order to form.

Carbon monoxide, as it bubbles off the bath, or as it exists as bubble in the bath, is probably at nearly atmospheric pressure. However, in order for that bubble to form there must have been present enough FeO and C to produce a considerably higher pressure. This explains, of course, why in the open hearth there is so much more of these two substances present than would be indicated by equilibrium conditions as measured by Mr. Kinzel.

Once it is started, more CO can diffuse into the bubble and produce a large bubble where the pressure is perhaps of normal magnitude. The pressure required to start may be in the neighborhood of 10 to 20 atmospheres. It is proportional to the surface tension of the iron and the best estimates of that quantity are very, very high—in the neighborhood of perhaps 25 to 30 times that of water.

Open-hearth men will agree with me that the bath of steel will tend to boil on anything solid put into it, such as the bottom or a rod or ore that is thrown in, and I think the answer is that any solid object acts as a nucleus for gas bubbles to form. There you have an analogy. The chemist in his laboratory uses glass beads in boiling point apparatus to avoid superheating. I think the rod that starts to boil in the open hearth is analogous to the glass beads.

C. H. HERTY, JR.—It is probably even more analogous to the time you got spattered in freshman chemistry when you had an evaporating dish, put in a stirring rod and had it pop out of the dish.

A. B. KINZEL.—I am interested in your refractory. What have you that will stand the slag?

J. M. GAINES, JR.—That tube was in the furnace for approximately 20 min.; a clay graphite tube made especially for the purpose; the bath was 0.22 per cent. carbon steel.

R. FRANCHOT, Washington, D. C.—Dr. Herty, why are you so certain that the reaction is reversible?

C. H. HERTY, JR.—For the simple reason that if there was no carbon and oxide at the start and CO was introduced carbon and oxide would be found in the metal.

G. E. THACKRAY, Bethlehem, Pa.—What is the connection between what you have just told us and the possibility of decarbonizing the heat to a certain extent without overoxidizing it? Where is that limit?

C. H. HERTY, JR.—That was the point I was going to develop. Sometime someone is going to find out how to get to equilibrium. Everyone else will be at a disadvantage, including the people who make deoxidizers. Once we find out why it takes so much oxygen in the metal to bring the carbon down, we can lower the amount of oxgen. By using a process other than open hearth we can bring carbon very low with very low oxygen. I think we can lower the present-day iron oxide content.

G. E. THACKRAY.—I am speaking as a melter who in the old days considered that there was a limit beyond which one could not go in attempting to reduce the carbon content of a heat, particularly with certain types of materials and certain brands of pig iron. If the attempt was made to reduce the carbon below a certain minimum the heat was overoxidized.

C. H. HERTY, JR.—If under certain conditions this high pressure of CO was necessary and could not be eliminated, we would have to overoxidize the heat with FeO to reduce the carbon.

G. E. THACKRAY.—To what point can you reduce the carbon without having what you might consider an undue amount of oxygen?

C. H. HERTY, JR.—We find in all the heats we have studied that there must be approximately 0.02 to 0.03 per cent. oxygen in the metal to get 0.08 to 0.10 per cent. carbon.

H. STYRI, Philadelphia, Pa.—Would it do any good to evacuate the furnace?

A. L. FEILD.—That is a pertinent question.

H. STYRI.—In connection with the pressure theory, it may be worth while to mention possibility of getting the gases out by poling. That is a practice used in copper refining.

A. L. FEILD.—To Mr. Franchot's question as to how we know the reaction was reversible, there are two answers, each one of which is adequate. One answer is in Mr. Kinzel's measurements. Most of them, in fact, were made from right to left. The second answer is that we know that CO is soluble in iron. This fact was not definitely known for many years. Since CO is soluble, it must tend to drive the reaction in the reverse direction.

SLAG ACTION IN LADLE

C. D. KING.—How does the slag action in the ladle differ between rimming steels and killed steels and why is there more danger of phosphorus reversion in killed steels?

C. H. HERTY, JR.—Relative to finishing the heat—on pages 276 and 277 of my paper[6] there is given a metal and slag analysis of a heat where the slag was sampled as the heat was going down the pouring platform. We got about 14 samples from the time the heat was tapped until the heat finishing pouring. That throws some light on what goes on in the slag after the heat is deoxidized.

[6] C. H. Herty, Jr.: Open-hearth Operation from the Chemical Viewpoint. See page 260.

First, in a rimming steel heat there is usually a little higher iron oxide than in killed steel heat; second, in rimming steel only manganese is added, and if aluminum is added it is only in small amount; third, the slags are somewhat thinner in rimming steel than killed after they get into the ladle.

In rimming steel iron oxide is diffusing into the metal from the slag and a ladle reaction is likely to occur if the slag is thin enough and the iron oxide high, and the temperature high enough. That would tend to give a ladle reaction.

On a killed steel the silicon and aluminum have taken considerable oxygen out of the metal, and in some cases have lowered the iron content of the slag and primarily made the slag more inactive than a rimming steel slag. In the particular slags shown on page 276, the first slag was taken as the heat was tapped. It was taken from the ladle at about the tenth ingot and showed a 10 per cent. rise in silica. The metal was rising in phosphorus, and manganese was dropping slightly. By the end of the heat the manganese oxide of the slag had increased considerably. The Fe_2O_3 had dropped considerably because there was no tendency to oxidize the slag. There was a crust of slag over the ladle so that the main body was not oxidized; the sulfur in the slag dropped, the sulfur in the metal rose and the manganese dropped.

All of this is tied up with the action of slag in the ladle. That is, a thin slag, high in iron oxide, will oxidize rapidly; a thick slag will oxidize very little.

The reason the metal in rimming steel should not be oxidized is that the aim is to control the amount of gas and in killed steel it is to keep as free as possible from inclusions.

Gases Given Off During Solidification

C. D. King.—What kind of gases are given off from an ingot of rimming steel during solidification and how do they differ from those given off from killed steel ingots? How do these gases affect the working of an ingot in the mill and what causes the formation of the various gases in the steel?

C. H. Herty, Jr.—Certainly the biggest problem in making rimming steel is that of gases in the steel, and in the killed steel, too. I would like to have Mr. McKune describe some experiments he made at Hamilton on gases coming from the ingots. In the first place, the four main gases are hydrogen, nitrogen, carbon monoxide and carbon dioxide.

It is easy to say that there are three sources of gas in steel: (1) if gases are dissolved in pig iron they are carried to the open hearth; (2) gases may be dissolved while oxidizing the scrap and while the scrap is running down into the bottom of the furnace; (3) CO and CO_2 come off as carbon is eliminated. Where most of the nitrogen comes, from, I do not know. Most of the hydrogen probably comes from the reduction of water vapor in the open hearth. Certainly most of the CO and CO_2 come from the oxidation of carbon during the heat. I believe we can say that they are the three sources of gas in the steel. How they come out and why is simply a question of solubility in a liquid and solid steel.

The diagram of Fig. 8, the only good solubility curve I know of gases in steel, was by Sieverts. He found that at the melting point of steel the solubility increased very sharply. It can be seen that if there is a saturated solution of hydrogen in steel at 1600° C. and the steel is solidified, the tendency is for considerable hydrogen to be given off. So the evolution comes mostly at the solidifying point. We know nothing about CO and CO_2. It will be difficult to measure them.

In the rimming steels, of course, in rimming in, the gases are given off from the surface and there results the familiar action of steel being swept up on the outside and carried down in the middle, and the rate at which the gases come off in the ingot mold is primarily what determines the properties of the rim-steel skin.

Mr. McKune has made a number of analyses of gas by capping ingots and collecting the gas and analyzing it. Lately he has been making volume measurements and he hopes soon to be able to say he believes he has accurate information on how much gas comes out of ingots of different sizes.

His work is the only work I know of that has been done on liquid steel, except that of Müller in Germany, who extracted the gases from an ingot by sealing the top and pumping off the gases. I think that determination was worthless except that it showed when the steel was evacuated the iron oxide reaction was promoted. He got off a tremendous volume of gas. I believe it was much too high for what was actually present in the steel.

F. B. McKUNE, Hamilton, Ont.—I have analyzed the gases coming off steel from 0.94 per cent. of carbon down to 0.05 per cent. They naturally vary, probably with the casting temperature and the time at which the test is taken. They all seem to vary according to the kind of steel that is being made.

On all of the analyses that we have run we have found no oxygen. These analyses were taken on different gases used in the open hearth, to see if it made any difference, but the gas analysis from steel made by producer gas, straight tar and straight by-product gas, making the same kind of steel, showed very little difference.

C. H. HERTY, JR.—A product tremendously more dense than obtained under present conditions would result. A rimming steel skin would approximate a dead killed steel casting as far as density is concerned.

F. B. McKUNE.—I have in mind a steel not deoxidized with aluminum, silicon or manganese or any other deoxidizer but in which the gases that are in the steel could be controlled below a certain point. We have found that where the gas analyses were lowest the steel showed up free from seams, slivers and blisters.

C. H. HERTY, JR.—There did not seem to be much relationship on the CO and CO_2 between the composition of steel and gas. There is a definite relationship between hydrogen and nitrogen.

F. B. McKUNE.—The analysis on the heat was 0.05 per cent. carbon, 0.03 sulfur, 0.18 manganese, 10 CO_2, 53 CO, 4.9 hydrogen, 31.7 nitrogen. On a 0.94 per cent. carbon, the silicon was 0.21; CO_2, 26; CO, 40; hydrogen, 21; nitrogen, 12 per cent.

C. H. HERTY, JR.—As the manganese in the steel goes up in the rimming steels, the percentage of hydrogen in the gas goes along with it, and the nitrogen drops off. I cannot see why that should be unless ferromanganese is fairly full of hydrogen, or high-manganese steel permits the release of hydrogen through the solid steel faster than does low-manganese steel.

G. B. WATERHOUSE, Cambridge, Mass.—Or else the liquid steel holds much more hydrogen than it gives up.

C. H. HERTY, JR.—You mean the solubility would be higher. That is very possible. I do not know how manganese or silicon affects the solubility of these gases. The CO and CO_2 do not seem to show anything definite with increasing manganese.

G. B. WATERHOUSE.—What is the Hamilton hot top?

F. B. McKUNE.—We think we have found the distance that a hot top should be put in the mold to eliminate piping. We use a split brick 1¼ in. thick and run it down into the mold for 15 in. We have found no pipe below this point.

A. B. KINZEL.—The matter of gases in steel came to my attention a few years ago. We found that the composition of CO and CO_2 coming off depended on the tempera-

ture at which the sample was taken and corresponded exactly to the equilibrium compositions which one would expect if CO and CO_2 were in equilibrium. It occurs to me that in gas analysis of steel ingots that is important. If the CO-CO_2 ratio is affected by the rate of cooling and rate of oxidation in the inside of the blowhole in which the particular gas happens to be held, an integration of the reactions results. The CO partly changes to CO_2 while the ingot is cooling.

A. L. FEILD.—It is interesting that the discussion has gotten around to the question of gases evolved from steels. We are all familiar with the fact that over a period of probably 20 or 30 years this question was about the only problem in the physical chemistry of steelmaking which was under discussion in the journals. In fact, Bessemer was the first to consider the problem. He put steel under a vacuum and found that a tremendous volume of gas was liberated, which he assumed was CO. Later an analytical method for gases was developed and results were published which showed there was practically no CO in steel. This fact was believed to have been confirmed by Müller. Still later, Stead and Richards stated that there was practically no CO in steel. These ill-advised conclusions practically killed Bessemer's original idea and kept back the development of the idea of the reaction between FeO and CO for many years.

It was not until about 20 years later, I think, that Snelus, at a meeting of the British Iron and Steel Institute, insisted he believed CO was soluble in steel. The work of Graham, who was the first to show that metals dissolved gases, came after Bessemer's work. It was principally on the strength of Graham's work that the erroneous views which had existed were revised. My own impression of this work on extraction of gases is that we are working at the wrong end, to analyze gases from steel without knowing what is going on in the steel while the gases are being evolved. I think Mr. Yensen can answer very well the question of what happens when steel is degasified with respect to CO.

T. D. YENSEN, East Pittsburgh, Pa.—Based on the recent work on gases in metals by Ziegler and others, and on the present views of solid and liquid solutions and of crystal structure, it is my opinion that gases obtained from solid and liquid metals are partly due to interaction between various elements present in the metal.

A certain amount of gas is probably present in the solid or liquid metal as gaseous elements or compounds. In the solid metal this is precipitated in the grain boundaries or even in the grains, like the more familiar solid or liquid precipitates Fe_3C, FeS, etc. In liquid steel it is uniformly distributed in molecular form and is probably the part that is first eliminated when the metal in the liquid state is subjected to vacuum treatment. With the metal in the solid state this part is not eliminated directly, except perhaps in the case of elements, like H_2, that can readily diffuse.

There is a certain solubility of carbon, oxygen, hydrogen, etc. in solid iron. My present view is that the atoms of these elements occupy interstitial spaces in the Fe lattice, diffusing from one lattice to another and in the course of events arriving at a grain boundary where they may interact with the precipitate found there. If given time, equilibrium conditions will be established between the dissolved atom and the precipitated elements or compounds, depending on the temperature and pressure. If the solid iron at an elevated temperature is subjected to vacuum treatment, so that the gaseous precipitates are removed from the surface, the equilibrium is upset, oxygen and carbon and other atoms from the interior will diffuse to the surface layer, combine and be removed as gas. The resulting decrease in the dissolved atoms will cause the intercrystalline precipitate partly to decompose into its elemental parts and these will dissolve in the metal and diffuse as described above.

At the grain boundaries and on the surface we may thus have FeO and CO, while carbon and oxygen atoms are found in the interstitial spaces of the Fe lattice, all

interacting under equilibrium conditions. Vacuum treatment will displace the equilibrium, carbon and oxygen atoms diffusing toward the surface where they will combine into CO and be removed, while more carbon and oxygen atoms will be formed in the interior from the FeO and CO precipitates until these are all used up, when the action will be carried on at a slower and slower rate by the dissolved atoms.

J. M. GAINES, JR.—One thing which impressed me in Mr. Zeigler's[7] paper was that in degasifying a sample, particularly the ones with considerable gas, he had to subject them in the liquid state to as high a vacuum as he could get for sometimes as long as two days. In talking about gases in steel and their effects, I believe we should keep in mind the fact that those gases may have been in the steel for a considerable period of time before we actually take the sample, and in order to get an answer to interpret our results, we have to go back in the process for possible sources of contamination with gas.

Recently, in working with electrolytic iron under an atmosphere of nitrogen, we have found that even after holding those samples for an hour in the liquid state and pouring in a chill test, they still showed signs of gas, which I believe is the hydrogen included in the manufacture of iron.

F. B. MCKUNE.—We have gone back to the heat in the furnace and got samples of gas. We were very careful to avoid having the pipe which we put down into the bath free from scale or other material that might create a gas. The pipe was fed into the bath as fast as it burnt off, as we were especially anxious to see if we could get some oxygen, which we did. We were trying to free the bath of gases before casting it into the molds. We are still doing a little of this and can report some progress along this line. It looks as though this is the place to start to remove these gases.

A. HAYES, Middletown, Ohio.—It seems peculiar that in the compositions Mr. McKune reports he gets essentially the same ratio of CO_2 to CO in the gases collected regardless of the composition of the steel in which he took them. This seems to indicate that there is a shift in the equilibrium between the CO and CO_2 as it is cooled from the temperature at which it comes from the steel down to the temperature at which he collected the gases. In other words, we know that in a 0.80 per cent. carbon steel at the temperature of the steel bath, the composition of gases CO and CO_2 in equilibrium with such metal contains an extremely small percentage of CO_2. If CO_2 is allowed to come to equilibrium at high temperature, the CO_2 content is extremely small, measured at atmospheric pressure.

Possibly this indicates that there is a shift in equilibrium during the extraction of the gases and may explain the fact that the gases obtained were of almost a constant CO-CO_2 ratio regardless of the composition of the steel.

This may be a very important factor in connection with sampling gases from any of the furnaces.

C. H. HERTY, JR.—I am afraid you misunderstood me. I did not say the ratio of CO to CO_2 was constant. I said it did not have any connection with the analysis of the steel. It varied considerably. I think you are right. There is no question that there is some change in composition.

A. HAYES.—We would expect the CO_2 content of gases in equilibrium with low-carbon steels to be much higher than the CO_2 content for 0.80 per cent. carbon steel at the temperature of ingot solidification.

A. L. FEILD.—I have made some calculations, which I hope are approximately correct. At high carbon contents, we can assume the gas contains practically 100 per cent. CO. On going down to very low carbon contents, as low as you can get in

[7] See page 428.

the open hearth, and assuming one atmosphere total pressure of CO plus CO_2, the figure is around 98 per cent. CO. A large CO_2 percentage must be due to the decomposition of CO in cooling or to oxidation.

T. D. YENSEN.—I think we should be careful when discussing gases in steel to try to keep in mind what actually may be going on in the steel. While some of the gas obtained from steel may actually exist as such in the steel, I think that the larger part is obtained through reaction between carbon and oxides when the pressure of the gas phase is reduced. This is shown by the reaction $FeO + C \rightleftharpoons Fe + CO$.

C. H. HERTY, JR.—Possibly it should be carbon plus FeO. That reaction is endothermic and the reaction $C + \frac{1}{2} O_2 \rightarrow CO$ is exothermic. When you ore a heat you immediately chill it. It can be frozen. Then, too, the slag of course has FeO in it. When you spoke about this reaction you were certainly talking about liquid steel. That is one way of saying the chances are you have FeO.

With a slag of various FeO contents, the oxygen content of the metal is proportional to the FeO content of the slag, which would indicate that FeO is dissolved in the metal. I do not believe the oxygen pressure is high enough to give as much oxygen as you find in steel.

A. L. FEILD.—We know the equilibrium dissociation pressures of gaseous CO and solution in iron should not change that at all, except for effect of the heat of solution of CO.

C. H. HERTY, JR.—As the temperature is raised most of these gases increase in solubility in steel.

J. JOHNSTON, New York, N. Y.—It does not matter what it is, as a matter of fact. It is the condition of equilibrium that is effective in a solution. We know little about what kind of molecules are present in a water solution and we know less about the silicates. We cannot reason at all from the things that come out of a solution as to what compounds existed in it in the liquid state. What comes out depends entirely on the *solubility* of the various things that might come out.

If you have a solution of magnesium carbonate in water and the CO_2 pressure is slightly above that of the CO_2 ordinarily present in the air (3 parts in 10,000), magnesium hydroxide is formed, if the reaction is effected slowly. The solution contains in fact a mixture of hydroxide and carbonate. You cannot make me believe that the composition of the solution changed suddenly as the pressure went from, let us say, 0.0004 atmosphere of CO_2 to 0.0002.

We must be very careful indeed about reasoning backwards from the solids we see coming from slags, when solidified, to what was present before solidification. In one sense it would not matter at all which equation is written as representing the change, if measurements that check the CO pressure against the oxygen content are obtained. This problem goes back to a question developed in all textbooks of physical chemistry. While the "activity," when more is known about it, may serve to interpret the actual situation, from a thermodynamic point of view it does not matter (within limits, of course) provided you make the appropriate measurements of the things you are trying either to increase or to decrease in the steel or slag effects.

A. L. FEILD.—In this connection, if you had these two equations, you get the one Dr. Herty has been speaking of, $C + FeO \rightarrow CO + Fe$. The equilibria of these two reactions have been measured up to about 1100° C., so it was those reactions which I used in calculating this equilibrium.

J. JOHNSTON.—That particular thing in other sets of reactions has been proved absolutely. If you do it right the result that you will actually obtain from the third

equation here by experimental determination will be indentical with what you calculate by a combination of the other two. Facts on equilibrium can never give you any information about mechanism. As soon as you start to apply thermodynamics, you are dealing with statistics entirely, not mechanism.

We have therefore much perfectly useless argument about mechanism when we are not really interested in it at all. We would like to know mechanism for rates of reactions, but when it comes to equilibrium it makes no difference whatever.

There have been some measurements of the gases that come from rocks, though I do not recall the exact data at the moment. Enormous volumes of gas are obtained from any rock hitherto tried. But the composition of the gas depends on the rate at which the rock is heated, indicating that there is a change between the various gases as the heating proceeds, and the speed with which the gas can diffuse out of the rock depends on the fineness of grinding.

In that particular case the presence of the gases makes an enormous difference on the viscosity of the liquid. Many lavas have flowed almost like water. Yet when remelted, lava forms a viscous liquid. That is because there were gases, principally water, that liquefied it. I should like to see more experiments on the effect of water on viscosity of slags. I know it is enormous.

I will give one example. The mineral albite melts at about 1200° C. It will not flow at all. Once albite is melted it will never crystallize. It stays as a glass. If it is melted in a single atmosphere of steam, it becomes a liquid as thin as water, and then recrystallizes immediately to albite again. There was certainly a difference of 10,000 times in the viscosity of that liquid, yet the amount of water in the liquid was only of the order of tenths or hundreths of one per cent. In one way, however, this statement does not give a fair indication of the large effect of water, because if we consider molecular concentration instead of gram concentration the concentration of water is fairly high, because albite has such a very high and water such a very low molecular weight.

Another point: If there is a virtual high pressure of CO preventing the reaction, it ought to be removed by the bubbling, giving an effect of one atmosphere right through. The conditions would be much the same as in glassmaking.

While it may be that the foam is dependent on the viscosity of the slag, it is certainly true that foam on water solution is not dependent on the viscosity of water to any great extent. The merest trace of a colloidal material will make all the difference between whether or not foam is formed, and the colloid certainly does not change the viscosity much. Saponin is put in all soft drinks to make them keep a foam.

I feel therefore that the surface tension of slags, liquid metals, etc., should be looked into because we will find it very important in some cases, but it is rather a difficult field to work in. It may quite well be that viscosity is the main factor, but we should not lose sight of the fact that surface tension may be equally important, and if it is, it would be affected in all probability by very small quantities of other things.

This explanation would account for facts that are observed in the case of two steels apparently almost alike but which behave differently. In one case we have an emulsifier and in the other we do not.

*

Open-hearth Operation from the Chemical Viewpoint*

By C. H. Herty, Jr.,† Pittsburgh, Pa.

(New York Meeting, February, 1929)

The reactions that occur in the basic open-hearth process are complicated and are subject to many different factors such as temperature, slag composition and rate of boiling of the bath. It is difficult, therefore, to present an extended theoretical discussion of open-hearth operations without confusing the theory of the process with the application of the theory. This paper attempts to present some of the theory of the open-hearth process without mentioning theory at any point, simply giving some of the practical applications of results founded both on theory and practice and on experimental work both in small and large furnaces. It is hoped that an answer to a number of questions commonly asked by the open-hearth operator may be found in this paper. Discussion of the subject matter is taken up more or less in the order in which a heat is worked, beginning with the oxidation of the scrap charged, sulfur absorption by the scrap, calcination of the limestone, and extending into the pig iron for the charge, the slags formed during the process, and some of the phenomena occurring in deoxidation of the steel and in its action in the molds.

Oxidation of Scrap

When scrap is charged into a furnace it immediately begins to oxidize. Oxidation is carried out by three reactions:

$$Fe + H_2O \rightarrow FeO + H_2 \text{ (absorbs heat)} \quad (1)$$

$$Fe + CO_2 \rightarrow FeO + CO \text{ (absorbs heat)} \quad (2)$$

$$Fe + \tfrac{1}{2}O_2 \rightarrow FeO \text{ (gives off heat)} \quad (3)$$

The product of oxidation contains some Fe_3O_4, but FeO usually predominates on account of the iron present in close contact with the scale formed. For a given type of scrap the amount of oxidation is controlled by the fuel and by the excess air being carried in the furnace, the temperature of the furnace, and the length of time that the scrap is in contact with the furnace gases. In general, less oxidation occurs when the furnace is run hot so that the scrap melts rapidly. More important in operation than the two variables atmosphere and temperature, is the type of scrap being

* Published by permission of the Director, U. S. Bureau of Mines. This paper was distributed in printed form at the Round Table on the Physical Chemistry of Steelmaking, and should be considered a part of the general discussion.

† Physical Chemist, Pittsburgh Experiment Station.

melted. Heavy scrap gives less oxidation than light scrap because it has less surface. The type of scrap and time for melting are the two major factors in oxidation of scrap. A detailed study of three heats[1] showed that during a period of 3½ hr. between charging and hot-metal addition, medium scrap gave 8.35 lb. FeO and heavy scrap 1.76 lb. FeO per 100 lb. scrap charged. Oxidation of scrap has an important bearing on the working of the heat, as high oxidation may cause the heat to melt "low" in carbon and low oxidation may cause it to melt "high" in carbon. If a uniform grade of scrap is provided, the amount of oxidation can easily be taken into account and the heat charged accordingly.

Sulfur Absorption by Scrap

While the scrap is melting, sulfur is being absorbed from the furnace gases or is being given up to the gas, depending on the amount of sulfur in both scrap and gas. Table 1 shows the amount of sulfur in the gas which is neutral to scrap of certain sulfur content. The sulfur in the gas is expressed in terms of sulfur in the fuel; if this latter is higher than that shown in Table 1, the scrap will absorb sulfur, whereas if the sulfur in the fuel is lower than that given in the table the scrap will lose sulfur to the gas. The further away the sulfur in the fuel is from the values given in the table the faster will be the absorption from high-sulfur fuels or loss of sulfur to the gases from the low-sulfur fuels.

Table 1.—*Sulfur Content of Gas Neutral to Scrap of Certain Sulfur Content*

Sulfur in Scrap, Per Cent.	"Neutral" Sulfur in Fuel		
	Coal (for Producer Gas), Per Cent. Sulfur	Tar or Oil, Per Cent. Sulfur	Coke-oven Gas; Sulfur, Gr./100 Cu. Ft.
0.02	0.38	0.40	97
0.03	0.49	0.51	123
0.04	0.59	0.61	150
0.05	0.67	0.69	169
0.06	0.73	0.75	183
0.07	0.77	0.79	194

This table shows that sulfur is almost always absorbed from producer gas unless unusually low-sulfur coal is used; that with oil containing 0.5 per cent. sulfur, desulfurization of the scrap will occur unless the scrap is very low in sulfur; and that raw coke-oven gas, which averages 450 gr. sulfur/100 cu. ft., should be cleaned to 123 to 150 gr./100 cu. ft. if sulfur absorption from the gas is to be avoided.

[1] C. H. Herty, Jr.: Basic Open-hearth Practice. *Trans.* Amer. Soc. Steel Treating (1927) **11**, 569.

Calcining the Limestone

As soon as the surface of the limestone comes up to about 900° C. (1652° F.) it begins to give off CO_2 fairly fast. Up to this temperature it has been giving off gas very slowly. A porous, open-grained stone calcines more rapidly than a dense stone, and the absorption of slag resulting from oxidation of scrap by the open-grained stone is also more rapid than by the dense stone. These two characteristics, faster calcining and faster slag absorption, determine to a considerable extent the character of the lime when it "comes up" during the lime-boil.

Pig Iron

Pig iron for the basic open hearth may be classified by its silicon and manganese content as follows:

Class of Iron	Si or Mn Content
1. Low-silicon iron	Under 0.80 per cent. Si.
2. Average silicon iron	From 0.80 to 1.40 per cent. Si.
3. High-silicon iron	Over 1.40 per cent. Si.
4. Low-manganese iron	Under 1.25 per cent. Mn.
5. High-manganese iron	Over 1.25 per cent. and averaging 1.60 to 1.75 per cent. Mn.

In the foregoing classification it is assumed that the usual sulfur and phosphorus contents of less than 0.05 and 0.30 per cent., respectively, are present, and the following discussion is limited to irons containing no unusual amounts of these two metalloids. Furthermore, it is obvious that classes 4 and 5 must be combined with classes 1, 2 and 3. A sixth class of iron, on which considerable discussion has centered during the past three years, is so-called "dirty iron." This iron may have a satisfactory chemical analysis, but the finished steel made from it is unsatisfactory as to quality. In the following discussion the effect of the various types of iron on open-hearth practice and product are pointed out.

Silicon in the Iron

All pig iron for the open hearth must contain some silicon. The reason for this is that phosphorus and sulfur, in the basic process, must be eliminated from the pig iron. Their elimination depends upon their passing from the steel into the slag as calcium phosphate and calcium sulfide. In order to hold these two compounds in the slag it is necessary that excess lime be present. If this were not the case they would revert to the metal and little or no elimination of phosphorus or sulfur could be expected. If the pig iron contained no silicon it would be very difficult to form a fusible slag which contained only lime, calcium phosphate,

calcium sulfide, manganese oxide and iron oxide without going to either a very high temperature or an excessive amount of iron and manganese oxides. Silica, SiO_2, formed by the oxidation of silicon in the iron, unites with lime to form a fusible slag. Such a slag will hold in solution the compounds mentioned above and, furthermore, will hold them in concentrations such that the steel will not be too rapidly oxidized by iron oxide, and calcium phosphate and calcium sulfide will be stable in the slag under ordinary operating conditions. As far as slag-making goes, silicon might be termed a necessary evil, because the presence of silica aids materially in removing phosphorus and sulfur by forming a

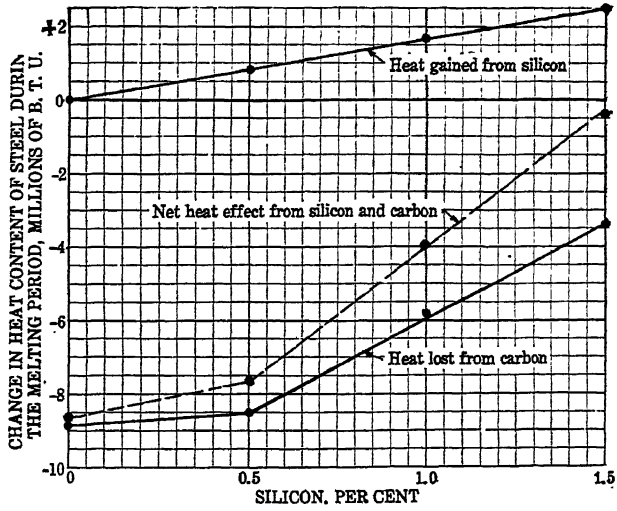


FIG. 1.—THERMAL EFFECT OF VARIATION IN SILICON IN PIG IRON IN CHARGE CONSISTING OF 40 PER CENT. PIG IRON, 60 PER CENT. SCRAP, 100,000 LB. TOTAL.

fusible slag with lime; at the same time silica makes it necessary to carry much more lime in the furnace than that needed simply to unite with the phosphates and sulfides formed in the bath.

Silicon serves one very important function; through its oxidation by reaction with FeO in the slag it deoxidizes the slags enough so that carbon is not eliminated too rapidly. The oxidation of silicon generates about 4170 B.t.u. per lb. of silicon, whereas the oxidation of carbon absorbs about 5400 B.t.u. per lb. of carbon. Thus the oxidation of silicon heats the bath and the oxidation of carbon cools the bath. It is common knowledge that the addition of ore when the heat is at too low a temperature is likely to freeze the heat on account of the great cooling effect of the carbon and iron oxide reaction.

The major function of silicon during the melting period is not only to generate heat in the bath but also to prevent the excessive carbon elimina-

tion which tends to freeze the heat, as the elimination of carbon absorbs heat from the steel. Fig. 1 shows the heat effect which would be obtained in a charge of 100,000 lb. carrying 40 per cent. pig iron, where variations in the amount of silicon in the iron are plotted against the net heat loss due to the oxidation of silicon and carbon. It has been assumed that variations in silicon in the iron cause the heats to melt as follows:

Si, Per Cent.	Heat Melts at Per Cent. Carbon
1.50	1.25
1.00	0.60
0.50	0.10

It will be noted that with low-silicon iron a very large cooling of the bath takes place because of carbon elimination, but that with high-silicon iron very little cooling takes place, not only because of the heat generated by the silicon but because of the small amount of heat lost through carbon elimination. If it were possible to have a pig iron containing 0.5 per cent. silicon and about 2.5 per cent. carbon, rather than one containing 4.0 per cent. carbon, the open-hearth furnace could be run much more easily on account of lessening the amount of heat absorbed in oxidation of carbon.

Low-silicon Iron.—One of the primary effects of low-silicon iron is a cooling of the bath so that reactions are slowed up; a great deal of excess heat must therefore be put into the bath through the gas during the early periods of the heat. If the low-silicon iron is put into the furnace after it has been charged for making normal silicon iron, the result is not only a cooling down of the bath and a charge which melts low in carbon, but also the production of excessively heavy slags which slow down the heat transfer from gas to metal, retard the elimination of the metalloids, and prevent a rapid elimination of the nonmetallic impurities in the bath. Unfortunately, with low-silicon iron the manganese content of the iron tends to drop, and this also assists in making poor slags during the early period of the heat.

With low-silicon iron it is often found that the slag is "dead" and inactive; this is caused primarily by its excessive thickness, but it is also due to the fact that the heat has been cooled down to such an extent through carbon elimination that diffusion of iron oxide from the slag into the metal is very slow and gives the furnace the appearance of being dead. The only way to remedy a dead slag resulting from low-silicon iron is either to thin the slag with spar or manganese ore (it is of course somewhat dangerous to use spar so early in the heat), or to heat the furnace so that the slag becomes fluid without the addition of a thinning agent.

With low-silicon iron it is often true that a heat will foam excessively throughout the melting period so that the roof is likely to be severely cut on account of the raising of the slag level in the furnace. There are two factors which cause heats to foam: (1) Very high surface tension of the slag will not allow the gases from elimination of carbon to work their way through the slag but will tend to hold them back and result in a foam which may raise the slag level in the furnace considerably. (2) The generation of more gas than usual per unit of time tends to raise the slag to a higher level than normal.

It has been noted in some experiments recently conducted in a small electric furnace that foamy slags are associated with high ratios of lime to silica in the slag. It is believed from the appearance of these slags and from their behavior on addition of small quantities of silica sand that there is a range of slag composition which is associated with very high surface tensions, so that when carbon is being eliminated rapidly, foaming is almost certain to result. The raising of the temperature of the bath may assist somewhat in reducing the foaming, but the foam in itself slows down the heat transferred from gas to metal so much that it is exceedingly difficult to get heat into the bath. Coal added to the slag sometimes assists in cutting down foaming, but this is usually only a temporary expedient.

The best method to correct foaminess is to change the slag composition so that it loses its high surface tension and allows the gas to escape freely; it is probable that the addition of silica to the slag would be of the greatest benefit. The silica could be added either as silica sand or preferably as silicon pig or ferrosilicon; these additions are of course expensive. The best way to eliminate foaming is to use a regular grade of pig iron in the furnace so that the slags formed during the melting period are of the correct composition. Unfortunately, so far as the writer is aware, few operators take the trouble to obtain slag samples during foamy periods. If a number of these samples were taken and analyzed, probably the procedure for correcting this condition could be easily determined.

High-silicon Iron.—As pointed out, high-silicon iron tends to heat the bath through its own heat of oxidation and through diminution of the heat absorption from the carbon reaction. The combination of high temperature and high fluidity of the slags resulting from heats of high-silicon iron often causes excessive erosion of the furnace lining. Furthermore, high-silicon iron deoxidizes the early slags to such an extent that the heats generally melt high in carbon, so that excessive time must be used in working the carbon down to the desired point. A large amount of silica in the slag necessitates the use of extra lime to make up the proper basicity; this slows down the furnace, inasmuch as heavy slag volumes slow down the rate of heat transfer from gas to metal. It is

the general rule that high-silicon iron gives thin slags during the working periods and low-silicon iron gives heavy slags. Fig. 2 shows the viscosity-composition relations of lime-silica slags. It will be noted that there is a sharp change in viscosity at 53 per cent. lime and 47 per cent. silica. In general, with iron fairly high in silicon the ratio of lime to silica in the

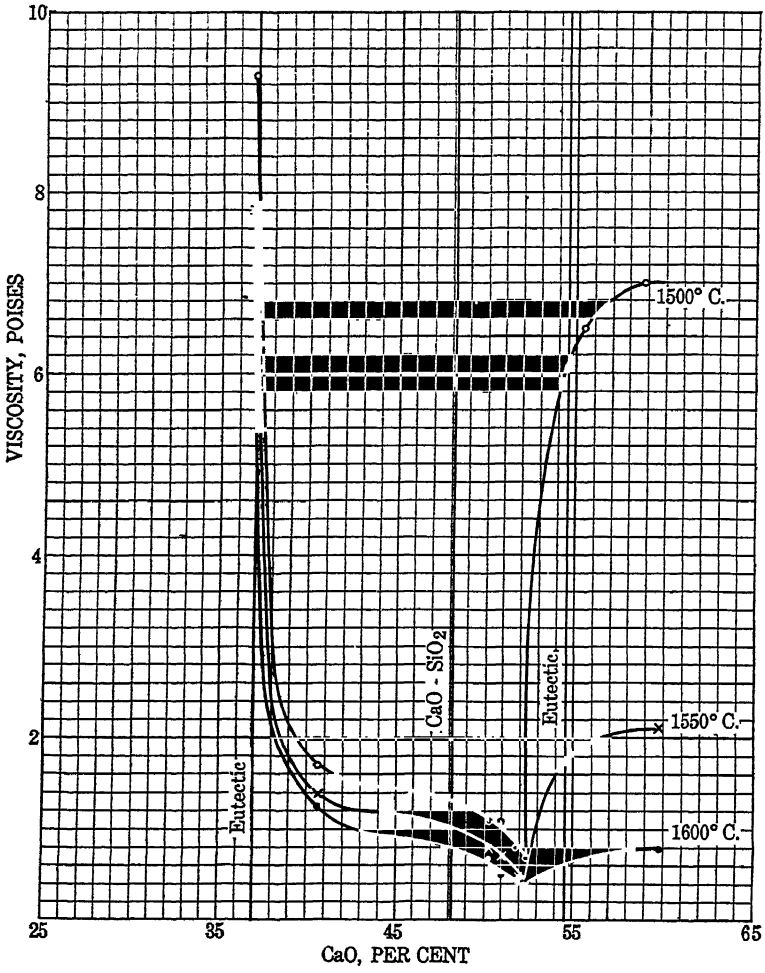


FIG. 2.—COMPOSITION-VISCOSITY RELATIONS IN CaO-SiO_2 SYSTEM.

slag during the lime-boil will be about 1:1; this results in a very fluid slag, as indicated in Fig. 2. On the other hand, with low-silicon iron the ratio of lime to silica is usually about 1.5 to 1; this condition results in a heavy viscous slag, as indicated in Fig. 2.

Obviously for regular open-hearth practice Fig. 2 can not be directly applied, because the open-hearth slags contain iron oxide and manganese

oxide, both of which tend to promote fluidity when added to calcium-silicate slags.

Manganese in Pig Iron

During the last five years open-hearth operators generally have begun to use high-manganese pig iron, which should be classed as iron containing 1.60 to 1.75 per cent. manganese, plus or minus 0.5 per cent. There are four distinct advantages in the use of high-manganese iron rather than low-manganese iron, as follows:

1. It is generally considered that the use of high-manganese iron in the blast-furnace charge smooths out the operation of the furnace to a considerable extent.

2. High-manganese iron acts as a protector for high-sulfur iron if the pig iron is handled properly after it leaves the blast furnace. It has been shown[2] that if the iron is held for a sufficient period and allowed to fall in temperature to about 2400° F., the product, per cent. manganese times per cent. sulfur, will equal 0.070. This means that if 2 per cent. manganese iron is being made, no matter what the sulfur content of the iron at the blast furnace, the sulfur content of the iron at the open hearth should be $\frac{0.070}{2}$, or 0.035 per cent. Proper handling of the iron means (*a*) that the temperature of the metal should drop enough so that the solubility of MnS will decrease and allow MnS to be thrown out of solution; (*b*) that sufficient time should be allowed for the manganese sulfide to rise to the surface of the pig iron in the ladle; and (*c*) that any sulfur-carrying slag should be skimmed off of the pig iron in the ladle and the mixer (if a mixer is used) as thoroughly as possible before putting the iron into the open hearth.

3. Although no quantitative data are available it is qualitatively true that the addition of manganese oxide to almost any slag will increase its fluidity. It is definitely known that the melting points of slags consisting of MnO and SiO_2 decrease as MnO increases up to 59 per cent. MnO. The melting point of this composition (59 per cent. MnO and 41 per cent. SiO_2) is 2175° F. It is also probably true for lime-silica slags that the addition of MnO lowers the melting points and at the same time increases the fluidity. Increase in fluidity is of great help in open-hearth operation in that it smooths out the operation of the furnace by making the slags more uniform throughout the heat rather than very heavy at one time and very thin at another. Uniform slag fluidity is highly desirable from heat to heat.

---

[2] C. H. Herty, Jr. and J. M. Gaines, Jr.: Unreduced Oxides in Pig Iron and Their Elimination in the Basic Open-hearth Furnace. See page 179.

4. High-manganese iron means high residual manganese in the open-hearth furnace. The increase in residual manganese can be calculated fairly closely from the relation

$$\frac{\text{Per cent. MnO in the slag}}{\text{Per cent. FeO in the slag} \times \text{per cent. Mn in the metal}} = 2.3 \qquad (4)$$

for normal open-hearth finishing slags, analyzing 14 to 17 per cent. silicon, 38 to 44 per cent. lime, and 0 to 3 per cent. P_2O_5. All that is necessary to calculate the residual manganese which will be obtained from a given increase in manganese in the charge is to know the approximate weights of slag and metal in the furnace. An example of this method of calculation follows:

Assume that the total manganese in the charge is 2300 lb., the metal weight 220,000 lb., the slag weight 25,000 lb., and the FeO content of the slag 20 per cent. These figures are derived from a charge containing 40 per cent. pig iron with 2 per cent. Mn in the iron and 0.40 per cent. Mn in the scrap.

Let

$$x = \text{lb. manganese in the slag,}$$

$$2300 - x = \text{lb. manganese in the metal,}$$

$$\frac{\text{MnO}}{\text{Mn}} = 1.29;$$

$$\frac{x}{25{,}000} \times 100 \times 1.29 = \text{per cent. MnO in the slag,}$$

$$\frac{2300 - x}{220{,}000} \times 100 = \text{per cent. Mn in the metal,}$$

$$20 = \text{per cent. FeO in the slag.}$$

Therefore equation (4)

$$\frac{\frac{1.29\ x}{25{,}000}\ (100)}{\frac{(2300 - x)}{220{,}000}\ (100)\ (20)} = 2.3.$$

Solving, $x = 1845$ lb. Mn = 2380 lb. MnO in the slag = 9.52 per cent MnO,

$$2300 - x = 455 \text{ lb. Mn} = 0.21 \text{ per cent. Mn in the bath.}$$

Fig. 3 shows how the residual manganese in the steel varies with the percentage of manganese in the charge and the FeO in the slag. The percentage of manganese in the charge is calculated on the basis that the scrap contains a constant percentage of manganese and that the manganese content of the pig iron varies. It can be shown theoretically that residual manganese has no effect on the iron-oxide content of the bath at

a given time, and that as the residual manganese increases the manganese oxide content of the bath must increase.

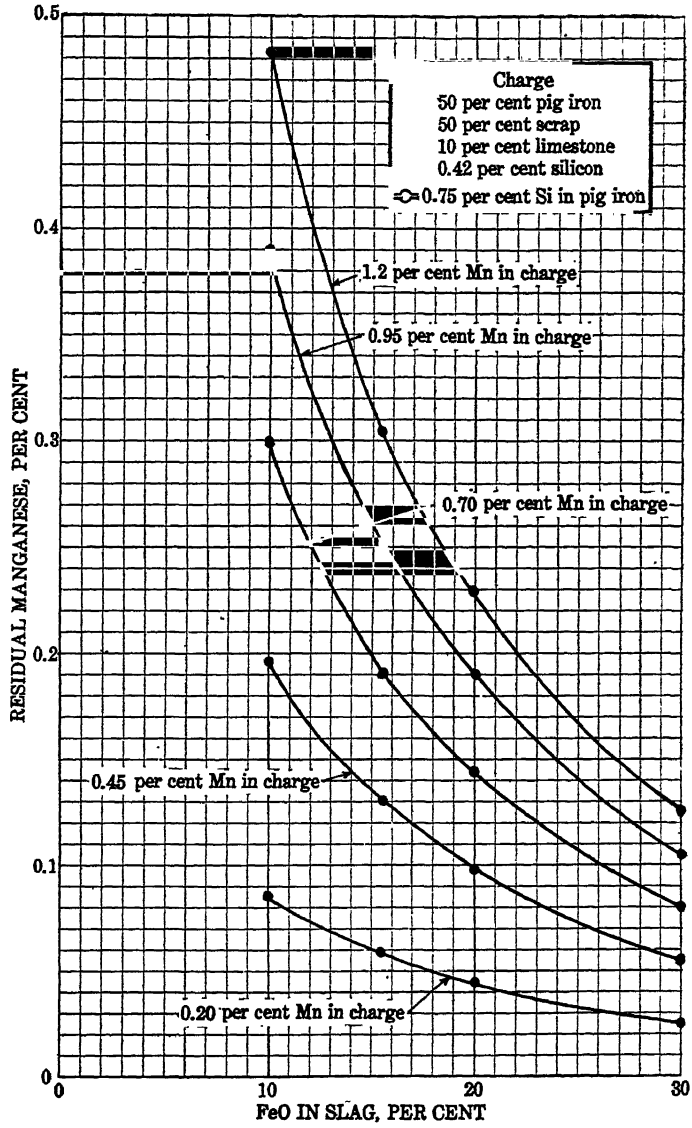


FIG. 3.—EFFECT OF MANGANESE IN CHARGE AND SLAG OXIDATION ON RESIDUAL MANGANESE.

It has been stated that if an excessively high residual manganese is carried, trouble is likely to occur in the surface of the finished steel. A possible explanation for this has been that an extra large amount of MnO might be present, resulting from the high residual manganese. This may

be true, but it is probable that very high residuals would have to be carried, say, 0.4 to 0.5 per cent. on low and medium-carbon steels and even higher than this on high-carbon steels. A recent investigation[3] has shown that as the residual manganese of the steel increases the amount of silicates in the bath decreases (Fig. 4). The effect of high residual manganese on the elimination of silicates is probably due to the MnO which is formed in the bath and acts as a flux on the silicates in the charge.

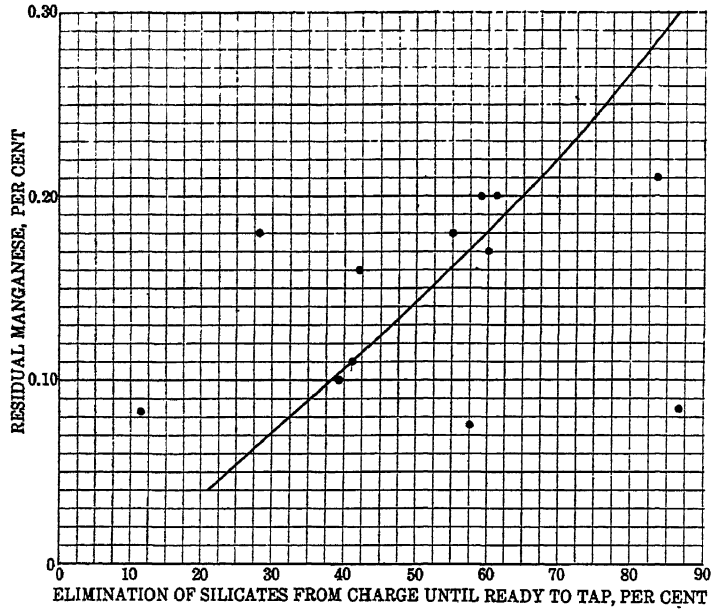


FIG. 4.—EFFECT OF RESIDUAL MANGANESE ON SILICATE ELIMINATION.

Oxides in Pig Iron

With reference to the class of iron known as dirty iron it can be stated that as blast-furnace operation becomes irregular the amounts of unreduced material in the pig iron increase. In general this unreduced material consists of very fine particles of silica and iron and manganese silicates. Some of these suspended materials are eliminated during the working of an open-hearth heat, but many of them remain in the steel throughout the process. Fig. 5 shows the relation between the SiO_2 in the charge (calculated from the SiO_2 content of the iron and the per cent. iron in the charge) and the amount of silicates in the tapping tests of a number of heats. It will be noted that there is an excellent relation between the amount of silicates present at the time of tap and the amount of silica present in the charge.

[3] Carnegie Inst. of Tech. *Bull.* 38; in preparation.

Slag during the Working Period

The composition of the slag during the working period depends on the composition of the pig iron charged, the amount of limestone charged, the oxidation of the scrap during melting, additions made to the slag during this period, and the amount of wear on the furnace lining and roof. With these five factors in mind it is small wonder that finishing slags vary considerably in chemical analysis from heat to heat.

For the purpose of this paper consideration will be given primarily to the iron-oxide content of the slag. Iron oxide is formed during the melting of the scrap, by oxidation of FeO to Fe_2O_3 in the slag by the furnace gases and by subsequent reduction of Fe_2O_3 by the metal bath;

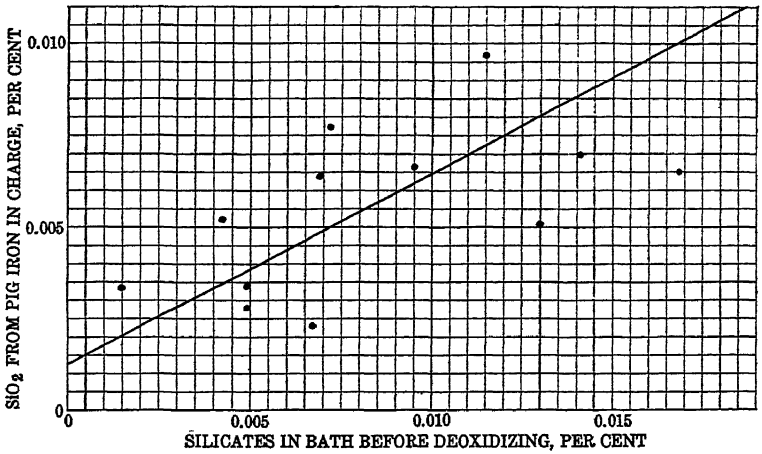


Fig. 5.—Relation between silicates in bath at end of heat and silica from pig iron in charge.

and by the addition of iron oxide either as ore or cinder. Iron oxide is eliminated from the heat by the oxidation of the metalloids carbon, silicon, manganese and phosphorus. The concentration of iron oxide in the slag will naturally depend on the amount of iron oxide formed and added during the heat, the rate of elimination of iron oxide by the metalloids listed, and the slag volume.

High concentrations of iron oxide are chiefly due to the excessive oxidation of scrap during melting and to overoreing of the heat. Similarly, excessively low concentrations of iron oxide may be formed from small amounts of oxidation during melting and underoreing of the heat. A third factor which will cause low iron oxide in the slag is the rapidity of the metalloid elimination, which may proceed so quickly that the iron oxide in the slag is depleted faster than it is formed by oxidation at the slag-gas surface. As already shown, the amount of iron oxide formed from heavy scrap is about 1.8 lb. FeO per 100 lb. scrap, and from medium-sized scrap

is about 8.3 lb. FeO. With small scrap the oxidation is probably higher than with medium-sized scrap, but not as high as would be indicated by the two figures given, for the reason that very small scrap tends to fuse over and form a fairly large surface after the furnace comes up to temperature rather than to continue exposing a large number of small surfaces, as is the case when the scrap is charged.

If the iron oxide content of the slag is high during the early stages of the heat it will probably stay high throughout the heat, because the only way it can be lowered is by depletion through oxidation of carbon or by a large increase in slag volume; the latter is an extremely undesirable condition. The adjustment of the iron oxide content of the slag is important because if too high or too low it may be injurious to the steel. If it is too high, excessively rapid oxidation of the steel will result and the steel will either be wild in the molds, as happens with rimming steel, or, as with killed steels, will contain an unusually large number of inclusions resulting from the oxidation of the deoxidizers added at the end of the heat. If rimming steels are being made, the iron oxide content of the slag may be so low that the rate of carbon elimination will be too slow for sufficient gas to be formed in the steel to make it rim properly. The correct iron oxide content of the slag will vary somewhat with the temperature of the bath. The higher the temperature the lower the iron oxide in the slag for proper rimming in the mold.

The proper fluidity of the slag is of great importance in regulating the rate of carbon elimination and the absorbing power of the slag for nonmetallic inclusions. If the slag is too heavy, carbon will be eliminated slowly and nonmetallics will not be properly absorbed. On the other hand, if the slag is too thin, carbon elimination will proceed too rapidly, and although inclusions may be absorbed by this type of slag, iron oxide will diffuse into the metal more rapidly than is desirable. Fluorspar is commonly used to thin heavier slags, but the use of high-manganese iron will cut down considerably the amount of spar necessary over a given period.

The mechanism of the thinning of slags by spar is not known. It is sometimes ascribed to the breaking down of some of the calcium silicates present in the slag with the formation of other calcium silicates or compounds which have a higher fluidity than those present before the spar was added. Whatever the cause, the effect of spar on a basic slag is to thin it considerably, and there is some danger in using spar in that oversparring will result in a slag so thin that large amounts of burnt lime are necessary to bring it back to the proper fluidity.

If extra lime is needed during the latter part of the heat, it is sometimes customary to add raw limestone instead of burnt lime to bring about the required increase in basicity. Raw limestone has the decided advantage of giving a boiling action to the bath through the evolution

of CO_2, but it also has the disadvantage, in some cases, of increasing the iron oxide content of the slag. This results from the two reactions

$$CaCO_3 \leftrightarrows CaO + CO_2, \quad (5)$$

and

$$CO_2 + Fe \leftrightarrows FeO + CO. \quad (6)$$

If the reduction of CO_2 to CO goes to completion as indicated by the above equations, 1.28 lb. FeO will be formed for every pound of CaO entering the slag. It can be easily seen that if raw limestone is used to bring up the lime content of the slag 3 per cent., the iron oxide content of the slag will immediately build up 3.9 per cent. because of the formation of FeO from CO_2 in the limestone. This may result in a more rapid carbon elimination than is desirable in some heats, and conversely may be of double benefit if the slag is too thin and carbon elimination is too slow.

Finishing the Heat

Rimming Steel

In finishing a heat of steel in the furnace there are three conditions to be met: If rimmed steel is being made it is desirable to have (1) the metal as clean as possible before tapping; (2) the proper temperature for mold conditions; and (3) the proper rate of carbon elimination so that the metal will rim well in the mold.

In order to clean the steel properly it may be deoxidized with alloys such as spiegel or silicon pig. The result is that the iron oxide content of the steel is temporarily lowered and the silica or manganese oxide formed will flux out impurities which come from the original charge. After this deoxidation the bath is held in the furnace until a reboil takes place; in making rimmed steel it is essential that a good full reboil be allowed to take place before the heat is tapped. Unless this condition is met the steel will generally rise in the molds and low ingot yield and steel of poor quality will result. When silicon is added to the bath the first product of the deoxidation is silica, SiO_2. This silica fluxes with FeO which is diffusing from the slag into the metal, forming fusible ferrous silicates which are eliminated from the bath.

The danger in adding silicon to a low-carbon heat of rimming steel is that some of the silica formed at first may not be completely fluxed by FeO and may remain in the steel up to the time of solidification. This causes what is known as dirty steel, with its subsequent effect on the rolling of the steel and on the quality of the finished product. It is better, in the writer's opinion, to use a deoxidizer such as spiegel or some other double deoxidizer which causes two products of deoxidation to be formed—in the case of spiegel, MnO and SiO_2. If these two deoxidation products are formed in the proper proportion they will immediately flux

together, forming fusible inclusions which are readily eliminated from the bath and "scrub out" other impurities as they rise through the metal into the slag.

The addition of silicon or spiegel to a heat raises the temperature, and it is often necessary with very cold heats to make such additions in order to get proper pouring temperatures; but it is far better to have a heat finish at the proper pouring temperature without the addition of any deoxidizer.

Rate of carbon elimination is largely controlled by the iron oxide content of the slag, the temperature, and condition of the slag. If carbon is being eliminated too rapidly the best way to finish off the heat is to cool the slag down so that diffusion of iron oxide takes place more slowly. The cooling can only be done, however, when the bath is sufficiently hot. If the iron oxide content of the slag is too high at the end of the heat, resulting in too rapid carbon elimination and large losses of manganese, the best way to reduce its injurious effects is to chill the slag in the ladle by the addition of coal, thereby cutting down the diffusion of iron oxide from slag to metal. Dolomite added to the ladle helps considerably in stopping the diffusion of iron oxide, but coal has the double effect of cooling in the same manner as dolomite and cooling by its reaction with iron oxide, and by actually lowering the iron oxide content of the slag.

Killed Steel

In making killed steel an entirely different condition must be met from that encountered in making rimmed steels. The heat may be killed either in the furnace or in the ladle; for this it is necessary to select the deoxidizer or deoxidizers for their deoxidizing effect not only on iron oxide but also on CO, and to choose deoxidizers so that the larger amounts of inclusions formed on deoxidation may be rapidly eliminated from the steel. In general, it may be stated that as the carbon in the finished steel increases it is better to use a deoxidizer with a high ratio of manganese to silicon. The reason for this is that high-carbon steels contain less iron oxide than low-carbon steels and that there is a point in oxygen content where manganese does very little deoxidizing. Thus it is possible that by using a silicon-manganese ratio of 1:1 during deoxidation the deoxidation product may be almost entirely silica, with very little manganese oxide formed, and this silica will not be eliminated from the steel before the metal is teemed.

If the heat is killed in the ladle the ratio of manganese to silicon is usually about 4 to 1, which may be sufficient to eliminate a great number of inclusions through the formation of a fusible manganese silicate. If, on the other hand, the bath could be killed in the furnace with a double deoxidizer which contained a ratio of manganese to silicon higher than 4

to 1, and the killing be then finished in the ladle, better results would probably be obtained. It is probable that in order to make the best grades of killed steels the heat should be killed in the furnace with a deoxidizer or deoxidizers which, upon reaction with the iron oxide in the metal, form fusible inclusions, and then finish the killing of the heat in the ladle after sufficient time has been allowed in the furnace for the products of deoxidation to be eliminated. Through this procedure the iron oxide content of the steel may be lowered considerably in the furnace so that the amount of nonmetallic matter formed in the ladle is reduced considerably over that which would be formed if the heat were killed entirely in the ladle.

Aluminum added to killed steels almost always forms Al_2O_3; this remains in the steel, unless the aluminum is added in combination with some other deoxidizer so that two oxides are formed simultaneously with the possibility of forming a fusible slag fairly high in alumina. It is often necessary to use aluminum in order to deoxidize the steel completely, as silicon alone is sometimes inadequate to accomplish this purpose.

Ladle Reactions

Rimmed Steel

As pointed out earlier in this paper, iron oxide is at all times diffusing from the slag into the metal. This process continues while the heat is in the ladle. If high iron oxide slags are carried in the furnace, large losses of manganese will result in the ladle unless the slag is heavy enough so that little diffusion of iron oxide takes place. Reactions are likely to occur if the slag is thin and high in iron oxide. Such reactions lower the carbon content of the metal considerably and cause wildness in the mold.

The basic slag reacts with the ladle lining and forms a ring of high-silica slag around the edge of the ladle; if the "pick-up" of silica is high enough it will cause considerable reduction of phosphorus into the metal. In most rimmed steel heats this kick-back of phosphorus is not encountered because the slags are high enough in iron oxide to prevent reversion of phosphorus.

Killed Steels

Slags from killed steels are lower in iron oxide than those from rimming steels on account of the reduction of iron oxide in the slag by the deoxidizers used. For this reason there is always danger that the phosphorus will kick back if the iron oxide is lowered too far and if the erosion of the ladle brick is excessive. In killed steels it is seldom that carbon is eliminated in the ladle, but silicon and manganese are often eliminated. If the silicon is high, little manganese will be lost, because the silicon will react with the iron oxide before the manganese will do so.

Figs. 6 and 7 show the changes in slag and metal composition on a heat of killed steel. The slag samples in these experiments were obtained by dropping a heavy weight attached to a cable into the ladle slag near the outer edge of the ladle at frequent intervals while the metal was being teemed, and then collecting the slag after each drop of the weight. It will be noted that the FeO in the slag decreases fairly rapidly, that the Fe_2O_3 in the slag is nearly eliminated, and that the SiO_2 content of the slag increases rapidly during the first part of the pouring process and remains

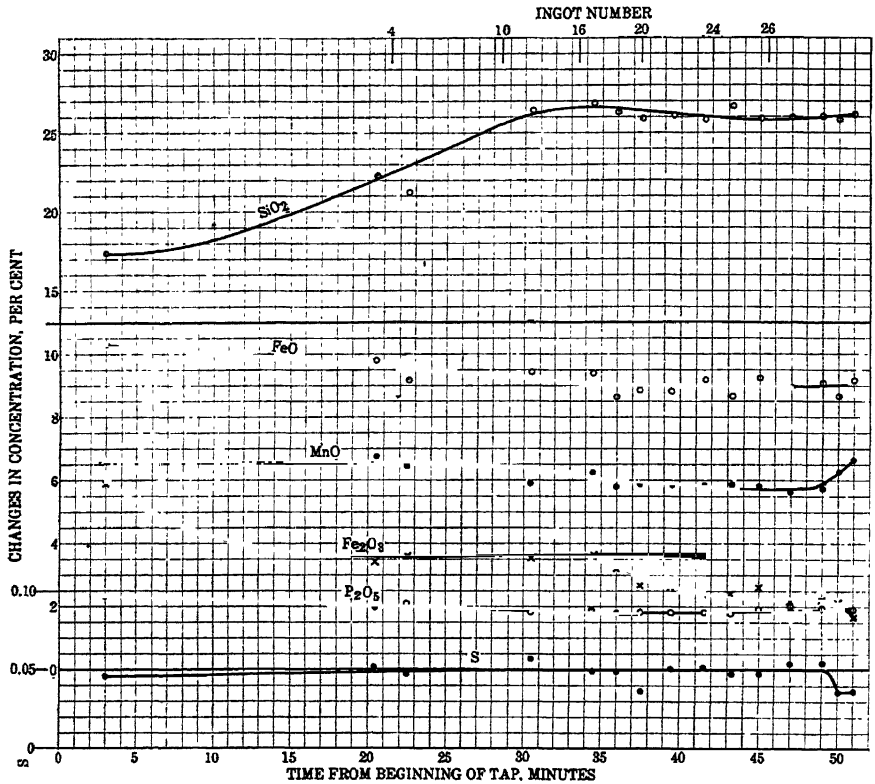


FIG. 6.—CHANGES IN CONCENTRATION OF SLAG CONSTITUENTS.

practically constant thereafter. The reduction in iron oxides is due to the deoxidizing action of the silicon and manganese, and the large decrease in Fe_2O_3 content is due to reduction of Fe_2O_3 by metallic iron and the deoxidizers. As there is no source of oxidation for the slag there is no tendency to form Fe_2O_3 from the FeO in the slag. The rapid increase in silica comes from the erosion of the lining while the slag is hot and in contact with the top layers of brick in the ladle. As soon as the metal begins to be withdrawn from the bottom of the ladle the slag has become cool enough so that little erosion of the lining takes place. Samples of

slag taken from the center of the ladle do not show such a rapid rise in silica, simply because the silica in the slag has not had time to diffuse from the outside edge to the center.

The last two samples in this series are of particular interest as they show the reactions that are taking place at the slag-metal surface. The manganese and phosphorus contents of the metal have dropped considerably and the sulfur content has increased. The elimination of manganese and phosphorus is favored by low temperatures. In this particular heat it is evident that the temperature at the slag-metal surface was low enough so that both of these metalloids were being

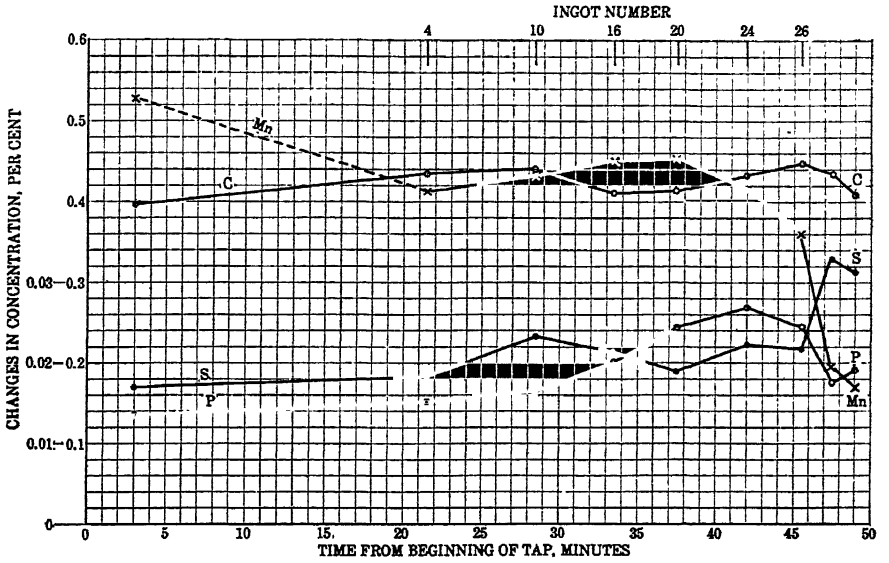


FIG. 7.—CHANGE IN CONCENTRATION OF METALLOIDS.

eliminated fairly rapidly at the slag-metal surface. The phosphorus had increased in the metal during the early part of the teeming, but equilibrium conditions shifted with the falling temperature so that at the end of teeming, phosphorus elimination took place instead of phosphorus reversion. The sulfur content of the steel increased at the same time because of the lowering of the basicity of the ladle slag.

Under severely oxidizing conditions it is probable that the last few ingots of a heat of steel will contain a great many more impurities than the first part, not only because oxidation at the slag-metal surface has been taking place throughout teeming, but also because inclusions which may have been well scattered through the steel when the heat was poured might concentrate in the upper layers of metal, making the last few ingots much dirtier than the main body of the heat. It is an experimentally determined fact that under certain conditions the percenta

of inclusions increases as the steel is withdrawn from the ladle; this is particularly true of killed steels.

Gases in Steel

The question of gases in steel has long been under investigation by almost every one connected with investigations of steel manufacture. The following comment was made by Pourcel[4] in 1882: "What is the gas which is evolved in abundance from the molds when the steel is on the point of solidifying? Sir Henry Bessemer answered that nearly 20 years ago." In spite of the fact that this question was answered 66 years ago it is apparent that there is still a great deal to be learned about gases in steel.

There are four gases which are given off from both rimming and killed steels, namely, carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), and nitrogen (N_2). The action of those gases in the solidifying steel controls to a considerable extent the surface of the finished product and, it is claimed by some, the physical properties of the finished steel. Unfortunately, most of the investigators who have dealt with gases in steel have confined their efforts to steel after it has been rolled and have used various methods to determine the amount and composition of the gases contained in the steel. The gases that cause so much trouble during rolling are not those dissolved in the solid steel but those which cause blowholes either just under the skin or in the interior of the ingot.

Sources of Gases in Steel

Gases in steel may be derived from three major sources: (1) They may be dissolved in the pig iron or in the scrap charged into the open hearth; (2) they may be absorbed by the steel during the period when it is exposed to the furnace gases, that is, during the melting period; and (3) they may be formed when carbon is eliminated. It is obvious that nitrogen in the steel must come from the nitrogen in the air, either in the blast furnace or the open hearth. The hydrogen in the steel must come from the reduction of water vapor by metallic iron; this water vapor either enters with the air and fuel or is the result of the oxidation of hydrogen or hydrocarbons in the fuel. Carbon monoxide, of course, is formed when carbon reacts with iron oxide. When the steel solidifies, these gases are given off in large amounts in the case of rimming steel and in small amounts in the case of killed steel.

---

[4] A. Pourcel: Notes on the Manufacture of Solid Steel Castings. *Jnl.* Iron and Steel Inst. (1882) 515.

A great part of the gases given off in rimming steel is driven out of the mold, but some of the gas is trapped by the solidifying steel; if enough gas is trapped the ingot will rise in the mold. One of the difficulties which would be encountered in making rimming steels with slags too low in iron oxide would be that carbon is eliminated very slowly under such a condition, and not enough gas would be formed in the steel to give the proper rimming action in the mold. There is a proper amount of gas which will give a good rimming steel, and an amount either smaller or greater than this will cause difficulties in rimming.

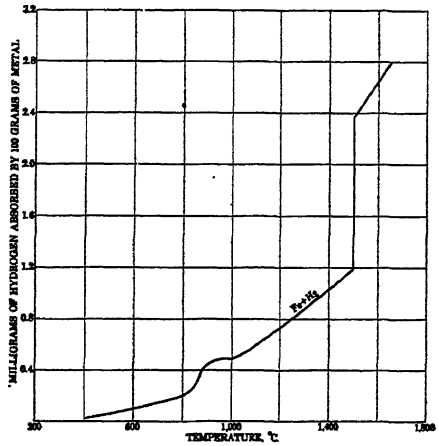


FIG. 8.—EFFECT OF TEMPERATURE ON SOLUBILITY OF HYDROGEN IN IRON (SIEVERTS).

The primary cause of excessive entrapment of gas is that the gas is given off so slowly that the brisk boiling action of the proper rimming steel is absent and the bubbles of gas at the surface of the solidifying steel are not swept away rapidly enough to prevent entrapment. The best way to avoid such a condition is to have a brisk enough evolution of gas; this is accomplished by having sufficient gas dissolved in the bath at the time the heat is tapped.

There are two primary causes for insufficient gas in the steel: (1) Too slow a rate of carbon elimination; and (2) a temperature so low that the solubility of the steel for gases is decreased. The solubility of hydrogen in steel has been determined by Sieverts[5] and is reproduced in Fig. 8. The large decrease in solubility at the solidifying point is clearly seen.

The best information on gases in rimming steel has been given by McKune.[6] He analyzed the gases coming from a number of ingots of rimmed and killed steels and found them to be of variable composition.

[5] Sieverts: *Ber.* Chem. Ges. (1910) **43**, 893; also Oberhoffer: Das Technische Eisen, 159. Berlin, 1925.

[6] Minutes of A. I. M. E. Conference on Open-hearth Steel Manufacture, Detroit meeting, Nov. 2–3, 1927 (1928) 22.

A retabulation of the data given by him has brought out the interesting point that as the manganese content of rimming steel increases, the percentage of hydrogen in the gas evolved increases and the nitrogen content decreases (Fig. 9). Pourcel, previously quoted, stated that the hydrogen content of steel increases with the manganese content in killed steels of 0.4 to 0.5 per cent. silicon. This high hydrogen content may be due to the solubility of hydrogen changing with the manganese content

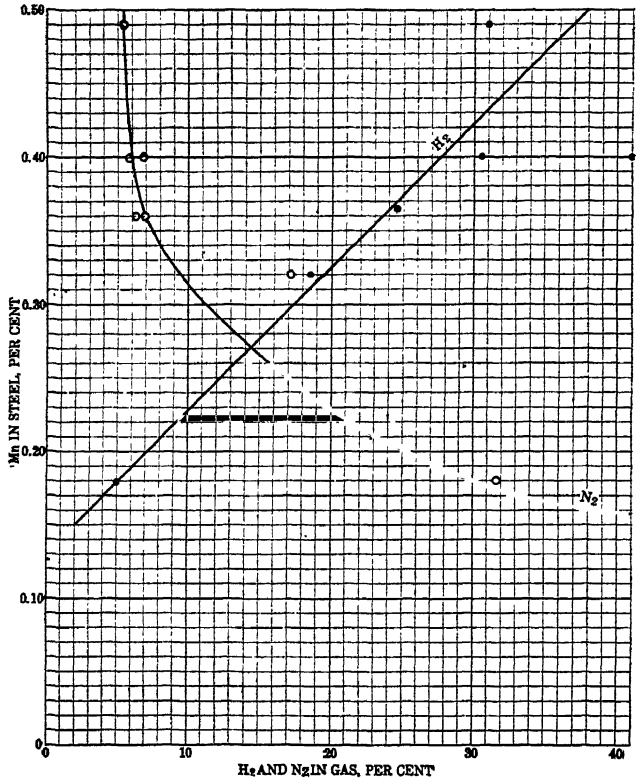


FIG. 9.—EFFECT OF MANGANESE IN STEEL ON COMPOSITION OF GASES EVOLVED DURING SOLIDIFICATION OF RIMMING INGOTS.

in the steel or to hydrogen contained in the ferromanganese. Unfortunately McKune's figures do not include total volumes of gas evolved but refer simply to the percentage composition of the gas. His data also show that the gases evolved from killed steels are much lower in CO and much higher in CO_2 than those evolved from rimming steels.

The gas issuing from a rimmed ingot 20 min. after it was poured contained more nitrogen and hydrogen and less CO and CO_2 than the gases evolved just after pouring the ingot. It is reasonable to suppose, therefore, that the blowholes in the center of the steel contained more hydrogen and nitrogen than the surface blowholes. The control of gases

in steel is a factor of extreme importance, and it is probable that the amount of hydrogen in the steel can be reduced by using a fuel low in hydrogen and drying the air for combustion, both in the blast furnace and in the open hearth. To obtain a real improvement in both hydrogen and nitrogen it would be necessary to make a detailed study of how these two gases were absorbed in the steel and how they could be eliminated by methods other than the present one of boiling them out with carbon monoxide.

Piping in Killed Steel

Piping in steel is caused by a contraction in volume when solidification takes place. Solid steel has a density of about 7.8 at ordinary temperatures; at the melting point the density drops to about 7.4, and as the temperature increases above the melting point the density decreases. Thus, whenever steel cools there is a tendency for the mass of steel to occupy a smaller volume than it did at its original temperature. In killed steels the top surface of the ingot solidifies soon after pouring has ceased and the shrinkage in the body of the steel results in a cavity known as a "pipe." The extent of piping will depend on the original temperature of the steel, the space occupied by blowholes in the ingot, and the rate of pouring, which are discussed below.

If any of the factors affecting piping tend to give a greater weight of steel per unit of volume in the mold at the end of pouring, piping will be diminished, and, conversely, if these factors give a smaller weight per unit volume, piping will be increased.

Original Temperature of the Steel

As pointed out, very hot steel has a low density; on solidification it would be expected to cause deep piping on account of the great difference in density of the solid and the high-temperature steel.

Blowholes in the Ingot

If the steel has definite large blowholes or contains a loose structure resulting from tiny gas holes, which show up in the rolled section as porosity, it will pipe less than dead-killed steel which contains no blowholes and has a truly dense structure. This is the reason that semikilled steel contains so much less pipe than steel fully killed.

Rate of Pouring

Obviously, if an ingot could be poured instantaneously there would be no solid metal at the end of pouring. If 10 min. were required to fill

the mold to the same height as in the case mentioned there would be a great deal of solid metal in the ingot at the end of the pour. This would result in having greater weight of steel in the same volume of mold than would be true if the mold were filled instantaneously. Slow pouring therefore favors small piping, and fast pouring favors deep piping.

Effect of Oxides in Steel

Although there is a great deal of speculation as to the effect of various oxides, nonmetallic impurities, in steel, the following statements are applicable to most grades of steel. Three possible sources of trouble during rolling and finishing may be considered: (1) Skin thickness will vary from ingot to ingot; (2) blowhole conditions in the steel will vary from ingot to ingot; and (3) cleanliness of the skin will vary from ingot to ingot. If we consider any two of these three variables as being constant in two ingots, it is almost certain that the thicker the skin of the ingot the fewer and the deeper the surface blowholes, and the cleaner the steel the better the ingot will roll. It would be entirely possible to have a very dirty steel which at the same time had a very thick skin with no surface blowholes and still have the ingot roll well. Conversely, it might be possible to have an extremely clean steel but one with a very thin skin and with an excessive number of blowholes near the surface and obtain a great deal of cracking during rolling. On the other hand, for a given thickness of skin the cleaner the steel is the better it will roll, and for a given number and depth of blowholes the better the steel will roll if it is clean. The three variables given can not be spoken of individually but must be considered together. Although dirty steel might be perfectly satisfactory under certain conditions, if the steel were uniformly clean the difficulties due to surface cracking would be considerably less.

In order to eliminate inclusions from the steel it is necessary to have a reasonably clean charge or have a slag of such composition and physical properties that the inclusions resulting from the charge will be largely eliminated. It is evident from general observation that simply increasing the fluidity of the slag is not always sufficient to eliminate inclusions, as there are times when regardless of the fact that a low limestone charge is being carried with resultant fluid slags the steel is not cleaned up as well as when extra lime is charged, or when either spar or high-manganese iron is used to obtain the required fluidity. A possible explanation of this situation is that high-lime slags have physical properties other than fluidity, such as surface tension, which are favorable to the absorption of nonmetallic matter and the resultant cleanliness of the steel. This is one question which can be answered only after a considerable amount of difficult experimental work.

In order to prevent the steel from having an excessive amount of inclusions it is also necessary that deoxidation be carried out carefully both in regard to the deoxidizers added and to the slag conditions in the furnace and in the ladle, as already outlined. If we consider nonmetallic inclusions only as far as the rolling mill is concerned, it is probable that they contribute considerably to the formation of seams and slivers simply on account of their tendency to weaken the steel while it is being rolled. This is certainly true in certain operations, such as the manufacture of seamless tubing, where an excessive amount of severe work is done on the steel, not only in straight deformation but in twisting the steel. Almost any type of inclusion, if enough is present, will cause failure under these conditions.

In speaking of inclusions the factor of free iron oxide in the steel must be mentioned. Many operators have the mistaken idea that a great deal of free iron oxide exists in finished steel. In killed steels it is seldom that more than 0.010 per cent. oxygen is present as iron oxide. The average iron oxide content of 18 samples of 0.08 per cent. carbon rimming steel was 0.051 per cent. (0.011 per cent. oxygen), and of 29 samples of 0.07 per cent. carbon bessemer rimming steel was 0.103 per cent. FeO (0.023 per cent. oxygen). Iron oxide in these amounts is probably soluble in the solid steel and would not be present as inclusions of iron oxide, so that its effect would not be the same as that of the sulfides and silicates which commonly occur in steel. It has been found that large amounts of iron oxide have little effect on the ultimate strength of steel, but they do have a marked effect on its elastic limit and impact strength. The extent has not been determined and little quantitative information is available on the effects of inclusions in the finished product. During rolling, most of the injurious effects of nonmetallic inclusions come from the insoluble particles such as the silicates and sulfides and from the refractory oxides, silica and alumina.

*

Diffusion of Iron Oxide from Slag to Metal in the Open-hearth Process*

By C. H. Herty, Jr.,† Pittsburgh, Pa.

(Cleveland Meeting, September, 1929)

The elimination of metalloids in the open-hearth process depends on oxidation of the metal by diffusion of FeO from the slag (or absorption of FeO by the metal), with subsequent reaction between dissolved iron oxide and the metalloids carbon, manganese, phosphorus, and silicon.

During an investigation on deoxidation with silicon, data on rate of oxidation of the metal were obtained, and these combined with certain other information, are presented here in an attempt to show the fundamental principles governing the diffusion of FeO from slag to metal. Inasmuch as the aim of the investigation was not a study of diffusion, certain data are lacking and it has been necessary to make assumptions on metal viscosity and effect of temperature on diffusion. These factors are known to exert a considerable effect on diffusional processes.

Overoxidation, or supersaturation of the metal with iron oxide, is not taken up in this paper. Overoxidation has little effect on diffusion except under a few special conditions, and the discussion has therefore been limited to diffusional processes.

Though the results given in this paper should be regarded as preliminary, certain of the conclusions drawn are definitely applicable to any steelmaking process.

Previous Study of Absorption

An extensive study of absorption has been made by the Department of Chemical Engineering, Massachusetts Institute of Technology. The results are of such direct interest in the problem of slag-metal reactions that it is felt worth while to summarize them here.

The following quotations are from Lewis and Whitman.[1] The reader need simply substitute "slag and metal" for "gas and liquid," with proper modifications to take into account the variations in physical properties of

* Published by permission of the Director, U. S. Bureau of Mines; the Carnegie Institute of Technology, and the Metallurgical Advisory Board.

† Physical Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[1] W. K. Lewis and W. G. Whitman: Principles of Gas Absorption. *Ind. & Eng. Chem.* (1924) **16**, 1215.

the phases. In the system under our consideration, slag and metal, both phases are liquids and we are therefore dealing with two liquid films instead of a liquid and a gas film.

> The basis of all processes involving the absorption or escape of gas lies in the fact that a liquid-gas system which is not in equilibrium tends to approach equilibrium conditions . . .
>
> Equilibrium or saturation represents the ultimate state which the system tends to assume, and is the first of the primary characteristics of absorption phenomena to be considered. The other fundamental is the rate at which the system approaches equilibrium, and in many cases the rate is more important than the equilibrium itself. These two factors are not independent of each other and, in general, the rate is greater the further the system is from equilibrium.

These authors consider that the main resistances to diffusion are offered by thin films at the surface of the liquids under consideration, in which concentration gradients are set up. In many cases of gas absorption it has been possible to calculate the thickness of these films and predict from the film thickness and the physical characteristics of the system the rate at which a gas will be absorbed in a liquid. In steelmaking the two liquids are slag and metal and the substance diffusing between them is iron oxide. The three controlling factors in rate of diffusion of this substance are the solubility relationship which controls the concentration gradients, the physical properties of the slag and the metal, and the thickness of the two films. From a consideration of the mechanics of absorption Lewis and Whitman stated that the ratio of viscosity to density of the film fluid was probably a controlling factor in determining film thickness, and conversely the ratio of density to viscosity would be a controlling factor in film conductivity.

Lewis and Whitman[2] cite three cases to show the controlling films in absorption of gases by liquids. If the gas is very soluble in the liquid, the liquid will absorb gas rapidly and the gaseous concentration at the interface will be small. In this case the gas film is controlling the rate of diffusion. With gases of very low solubility only small concentration differences can be established across the liquid film. In this case the gas film may be neglected and the liquid film will be controlling. With gases of intermediate solubility both films may be factors in controlling the diffusion rate.

With pure gases there will obviously be no concentration gradient through the gas film, and the liquid film will be entirely controlling. Inasmuch as FeO is fairly soluble in iron, both films must be taken into account; but from considerations of viscosity, as shown later, it is probable that the slag film offers the greatest resistance to diffusion of FeO from slag to metal.

---

[2] W. K. Lewis and W. G. Whitman: *Op. cit.*

Diffusion Equations

The amount of FeO diffusing per unit of time from slag to metal must obviously pass through both the slag and the metal film, and the rate at which it passes through will be proportional to the area for diffusion, to the concentration gradients in the films and to the physical characteristics of the films. If we call $\frac{dW}{d\theta}$ the amount of FeO diffusing per unit time and A the area for diffusion (in this case the slag-metal surface, or the active portion of it), the equation for absorption (or diffusion) is:

$$\frac{dW}{A\,d\theta} = k_s(\mathrm{FeO}_{\mathrm{slag}} - \mathrm{FeO}_{\mathrm{interface}}) = k_m(\mathrm{FeO}_{\mathrm{interface}} - \mathrm{FeO}_{\mathrm{metal}}) \qquad (1)$$

where k_s = diffusion coefficient through the slag film;
k_m = diffusion coefficient through the metal film;
FeO = concentration at the point indicated by the subscripts.

If the solubility relationships are known over the range of temperature and concentration being studied, it is possible to use an over-all coefficient so that only the concentration in the slag and metal must be known. This relationship has been determined[3] and the over-all diffusion equation may be written

$$\frac{dW}{A\,d\theta} = K_s(\mathrm{FeO}_{\mathrm{slag}} - \mathrm{FeO}_{\mathrm{metal}}), \qquad (2)$$

where the metal concentration is expressed in terms of the slag by the solubility relationship and K_s is the overall coefficient based on the use of slag concentrations, and

$$\frac{dW}{A\,d\theta} = K_m(\mathrm{FeO}_{\mathrm{slag}} - \mathrm{FeO}_{\mathrm{metal}}), \qquad (3)$$

where the slag concentration is expressed in terms of the metal by the solubility relationship and K_m is the over-all coefficient based on the use of metal concentrations.

The over-all coefficients may be calculated from the two film coefficients by combining equations (1), (2) and (3) with the solubility relationship,

$$H = \frac{\text{FeO in the metal}}{\text{FeO in the slag}}. \qquad (4)$$

The equations combining the over-all and film coefficients are:

$$K_s = \frac{Hk_mk_s}{Hk_m + k_s} \qquad (5)$$

and

$$K_m = \frac{K_s}{H} = \frac{k_mk_s}{Hk_m + k_s}. \qquad (6)$$

The data obtained in the study of deoxidation with silicon are not sufficient to evaluate the two film coefficients, but the over-all coefficients

[3] C. H. Herty, Jr. et al.: The Physical Chemistry of Steel Making: The Solubility of Iron Oxide in Iron. Carnegie Inst. Tech. *Bull.* 34 (1927) 68 pp.

may be readily calculated and the effects of the above mentioned variables qualitatively shown.

From the standpoint of open-hearth operation the two most important points to be learned from a study of these equations are: First, if the two film coefficients can be determined a method is available for determining the iron oxide concentration at the interface, a point of direct interest in studying oxidation of the metal and elimination of nonmetallic matter by fluxing as well as a fundamental factor in studying the equilibria of the metalloids. Second, the equations give a quantitative method of studying the effect of agitation, slag viscosity, and bath dimensions on the working of open-hearth heats.

As discussed above, the diffusion of iron oxide from slag to metal is probably controlled by the resistance of two liquid films, a slag film and a metal film at the interface between slag and metal. These resistances are determined by the character of the slag and metal, and by the physical action in the bath.

Velocity and Agitation

Haslam, Hershey and Keen[4] have shown that when sulfur dioxide and ammonia are dissolved in water, the gas-film coefficient is proportional to the 0.8 power of the gas velocity. In other words, if the gas rate is doubled the amount of absorption increases 74 per cent., because the gas film is thinned by the sweeping action of the gas stream. The same effect would be expected of the liquid film if the velocity of the liquid past the interface were increased.

The effect of stirring on the thickness of liquid films has been shown by numerous investigators and some of the results are summarized by Lewis and Whitman.[5] Correlation of data of investigators who have studied the absorption of gases in liquids by stirring the liquid at various rates is summarized in the following table. In all cases the absorbing liquid was water.

Speed of Stirrer, Revolutions per Minute	Gas Being Absorbed	k_1	Film Thickness, Cm. Calculated
At rest	O_2, N_2	0.4	0.17
60	O_2	3.3	0.020
150	O_2, N_2	5.0	0.013
250	CO_2	7.5	0.009
1000	O_2, N_2	15.0	0.0045

[4] R. T. Haslam, R. L. Hershey and R. H. Keen: Effect of Gas Velocity and Temperature on Rate of Absorption. *Ind. & Eng. Chem.* (1924) **16**, 1224.

[5] W. K. Lewis and W. G. Whitman: *Op. cit.*

Different types of vessels and stirrers were used in the experiments listed above. Becker's data[6] using one type of stirrer show that the coefficient increases almost proportionally to the 0.8 power of the velocity of rotation, checking the results obtained by Haslam.

The effect of agitation is twofold; the liquid films are thinned as by stirring, and the effective area for absorption is increased.

During the lime boil in the open hearth it could be expected that the films at the point where the lime boil is strong would be thinned considerably, and in the case of strong boils, the films might conceivably be ruptured with consequent rapid increase in the rate of diffusion of FeO into the metal. When a heat is killed with silicon and then reboiled, the action on the bath gradually increases until normal carbon elimination takes place. The surface films are thick while the metal is dead and gradually thin out as agitation by CO evolution commences, with consequent movement in the metal.

Viscosity

Haslam, Hershey and Keen[7] in studying the absorption of SO_2 and ammonia in water found that the film coefficients were proportional to the $\frac{2}{3}$ power of the ratio $\frac{\text{density of liquid}}{\text{viscosity of liquid}}$, thus verifying Lewis and Whitman's statement and giving quantitative information on the effect of viscosity.

For open-hearth work we are thus supplied with information which makes it certain that increased slag viscosity will decrease the rate of diffusion and with it the rate of carbon elimination, a fact commonly known to every open-hearth operator. The important point is that not only does the slag viscosity affect the rate of diffusion but the same is true of metal viscosity, and we have a method of quantitatively determining the effect of each, once the proper data have been obtained.

Temperature

Aside from the effect of temperature on slag and metal viscosity there is the important effect of the temperature coefficient of diffusion. We would expect that at 1600° C. diffusion coefficients would be much higher than at room temperature. Öholm[8] found that the temperature coefficient of diffusion, α, varied inversely as the diffusion coefficient itself—

[6] H. G. Becker: A Simple Form of Apparatus for Observing the Rate of Reaction Between Gases and Liquids, and Its Use in Determining the Rate of Solution of Oxygen by Water Under Different Conditions of Mixing. *Phil. Mag.* (1923) **45**, 581.

[7] R. T. Haslam, R. L. Hershey and R. H. Keen: *Op. cit.*

[8] L. W. Öholm: Ueber die Hydrodiffusion der Elektrolyten. *Ztsch. Phys. Chem.*, (1904) **50**, 309.

L. W. Öholm: Die freie Diffusion der Nichtelektrolyte. *Ztsch. Phys. Chem.* (1910) **70**, 378.

that is to say, the higher the diffusion coefficient the lower the value of α. Inasmuch as we have no data at room temperature on the diffusion of iron oxide it is difficult to predict how the open-hearth coefficients should compare with those found in liquids at room temperature. If we use $\alpha = 0.020$, given by Öholm for fairly high diffusion coefficients, we find by substituting in his equation

$$\frac{D_2}{D_1} = 1 + \alpha(T_2 - T_1)$$

$$T_2 = 1600° \text{ C.} = 1873° \text{ C. abs.}$$

$$T_1 = 20 \qquad = 293$$

that $\frac{D_2}{D_1} = 32.6$. If this value is a fair approximation we should find the coefficients in the open hearth about 30 times as high as those given by Lewis and Whitman.

Unfortunately, data whereby we may calculate α for the range 1500 to 1650° C. are lacking so we can not estimate the effect of temperature in this range.

Nomenclature

$\frac{d\text{FeO}}{d\theta}$ = lb. FeO absorbed per minute.
A = slag-metal area in square feet.
k_s = diffusion coefficient through the slag film.
k_m = diffusion coefficient through the metal film.
FeO_s = concentration of FeO in the slag, mol fraction.
FeO_m = concentration of FeO in the metal, per cent.
H = solubility coefficient, per cent. FeO in the metal divided by mol fraction FeO in the slag.
K_s = over-all diffusion coefficient, based on slag concentrations.
K_m = over-all diffusion coefficient, based on metal concentrations.

Data

The data used in this work were obtained in four sizes of basic open-hearth furnaces, as follows:

Heats	Tons	Hearth Dimensions		Slag-metal Area, Sq. Ft.	Carbon in Finished Steel, Per Cent.
		Length, Ft.	Width, Ft.		
K, J, N, P, U	40	22	13	195	0.10
W, X	75	30	14	305	0.80
Q, R, V	90	34	14	345	0.18
B	100	39	14.5	429	0.10

No determinations of FeO in the metal were made on heats *B*, *W* and *X*. However, in the investigation on deoxidation with silicon, preliminary results indicate that the iron oxide content of the bath may be

calculated fairly closely by the relationship (C)(FeO) = 0.0080, when carbon and FeO are expressed as weight per cent. In all cases where the FeO content of the bath has not been determined, it has been estimated from this relationship.

The metal temperature was calculated by the use of the manganese equilibrium constant.[9] Slag viscosities were determined by means of the inclined plane method. In this method a sample spoon is well slagged, then filled with slag and withdrawn from the furnace. The slag is immediately poured down an inclined plane, the angle being 30° with the horizontal, the thickness of the slag layer on the plane at a distance 1 ft. from the top being taken as a measure of the slag viscosity. The viscosity is reported in inches, and as will be brought out later can be compared with the true viscosity with good accuracy.

Tables 1 and 2 give the data from which the diffusion constants have been calculated. Where there are two sets of data per heat, the first refers to the period before the silicon addition, the second to the reboil after the silicon addition, except on heats *B*, *K* and *X*. In heat *B*, periods 1, 2, 3, 4 and 6 were normal operation, except as noted, and period 5 was immediately after a small hot-metal addition. In heat *X* all three periods were normal operation. In the heats killed with silicon the subscripts *w* and *r* are used to denote the working period before the silicon addition and the reboil respectively.

The two periods in heat *K* were immediately after adding spiegel and cold pig iron.

Slag and Metal Viscosity

The three major factors, aside from agitation, in determining the values of K_s and K_m are slag and metal viscosities and the temperature coefficient of diffusion. As pointed out previously, the last quantity cannot be determined at present.

The inclined plane method of measuring viscosity has recently been compared[10] with true viscosities by measurements of viscosity by the torsion method and the plane method on identical slags. The results of the preliminary experiments on the comparison are shown in Fig. 1, which has been extrapolated to include the range covered in the open-hearth heats. In the discussion of the diffusion coefficients the true viscosity of the slag in poises will be used, these values being read from Fig. 1 from the measurements on the plane. It should be noted here that of the two heats having plane viscosities of 0.25 in., only one was a direct measurement, heat *J*. No plane viscosities were taken in heat *U*, but the slag was noted as being "thick and puffy." The slag in heat *Q* was too thick to measure and has been given the value of 0.30 simply to

[9] C. H. Herty, Jr. et al: *Op. cit.*

[10] Bureau of Mines investigation in progress.

TABLE 1.—*Original Data for the Calculation of the Diffusion Coefficients*

Heat and Time		Metal, Per Cent.			Slag, Per Cent.								Mol Fraction FeO[b]	Temperature Calculated, Deg. C.[b]	Tapping Temperature, observed, Deg. C.	Slag Viscosity, inches[b]	Remarks
		C	FeO[a]	Mn	FeO	Fe_2O_3	MnO	SiO_2	P_2O_5	CaO	MgO	Al_2O_3					
B-1	6:40	0.486	0.017[d]	0.20	10.0	3.00	8.0	16.5	2.5	50.0	5.8						
	7:00	0.342	0.023[d]	0.16	11.7	5.8	9.1	16.5	3.3	44.3	5.8		0.180	1571		0.162	Ore at 6:25.
B-2	7:00	0.342	0.023[d]	0.16	11.7	5.8	9.1	16.5	3.3	44.3	5.8						
	7:15	0.272	0.029[d]	0.15	10.9	5.7	8.5	16.4	3.0	45.1	6.1		0.202	1577		0.138	Normal working.
B-3	7:15	0.272	0.029[d]	0.15	10.9	5.7	8.5	16.4	3.0	45.1	6.1						
	7:30	0.223	0.036[d]	0.19	10.2	5.6	8.0	16.4	2.9	46.9	6.5		0.196	1590		0.192	Normal working.
B-4	7:40	0.155	0.052[d]	0.18	11.0	7.5	7.3	15.8	2.7	47.3	6.2						
	8:00	0.085	0.094[d]	0.18	11.9	5.5	7.5	15.3	2.6	47.7	6.1		0.205	1608		0.152	Normal working
B-5	8:15	0.181	0.044[d]	0.17	11.3	4.5	7.3	15.4	2.4	47.6	6.1						
	8:30	0.140	0.057[d]	0.20	11.0	4.7	7.1	15.0	2.3	47.6	6.1		0.180	1594		0.207	8000 hot metal at 8:09.
B-6	8:30	0.140	0.057[d]	0.20	11.0	4.7	7.1	15.0	2.3	47.6	6.1						
	9:00	0.090	0.089[d]	0.17	11.9	7.1	6.6	14.5	2.3	47.5	6.2		0.193	1611		0.169	Normal working.
J	1:55	0.207	0.039[d]														
	2:12	0.130	0.062[d]	0.09	15.3	4.08	6.27	17.88	2.40	35.4	9.3	3.48	0.247	1565		0.25	After ore addition.
	2:31	0.110	0.073[d]														
	2:37	0.080	0.100[d]	0.060	14.55	8.81	5.28	16.90	2.14	36.4	12.1	2.88	0.272	1570	1570	0.12[c]	During reboil after silicon addition.
K	9:18	0.100	0.081[d]														
	9:27	0.060	0.135[d]	0.12	11.14	4.57	6.22	21.88	1.66	35.6	12.94		0.203	1585		0.15	After spiegel addition.
K	9:30	0.100	0.125														
	9:35	0.070	0.103	0.12	12.81	4.94	6.14	20.16	1.60	36.0	11.97		0.208	1602	1580	0.125	After cold pig addition.
N	2:03	0.270	0.030[d]		27.4	4.95	5.63	17.16	2.31	31.58	9.75						
	2:22	0.140	0.112	0.083	15.7	5.53	5.80	19.16	2.94	38.36	11.55		0.298	1590		0.07	After ore addition.
N	2:46	0.082	0.121														
	2:52	0.052	0.148	0.078	17.3	5.10	5.38	18.40	2.29	38.27	12.37		0.254	1600	1675[c]	0.12[c]	During reboil after silicon addition.

P	5:24	0.216	0.058													
	5:39	0.140	0.075	0.078	12.4	4.10	6.13	21.00	2.13	39.10	11.30		0.223	1555		0.08[e]	After ore addition.
P	5:56	0.098	0.081													
	6:04.5	0.060	0.139	0.064	16.6	5.95	4.56	18.22	1.94	36.80	13.20		0.258	1591	1700[e]	0.08	During reboil after silicon addition.
Q	11:11	0.156	0.063		12.7	10.4	4.16	15.78	1.49	44.2	7.30						
	11:51	0.071	0.108	0.073	15.8	7.54	4.53	15.10	1.37	42.7	8.14		0.255	1604	1600	0.30[e]	During reboil after silicon addition.
R	8:44	0.318	0.016		12.7	2.73	8.50	23.95	1.87	33.57	12.34						
	9:33	0.180	0.029	0.093	11.9	3.50	7.30	20.98	2.02	38.50	10.17		0.196	1534		0.12	Normal working.
R	10:02	0.172	0.016														
	10:16	0.104	0.081	0.100	12.8	3.6	6.05	21.08	1.97	38.90	10.50		0.196	1572	1585	0.135	During reboil after silicon addition.
U	6:15	0.104	0.061														
	6:22	0.061	0.085	0.086	17.65	9.28	6.18	14.92	2.21	39.05	9.40	2.20	0.305	1610	1631	0.25[e]	During reboil after silicon addition.
V	9:25	0.178	0.031		10.2	8.30	3.59	17.76	1.92	47.15	8.70	2.66					
	9:43	0.125	0.081	0.070	14.1	6.19	4.03	17.94	1.71	43.35	9.32	2.44	0.234	1605	1610	0.19	During reboil after silicon addition.
W	10:20	0.935	0.009[d]	0.34	10.6	7.9	12.3	16.3	2.9	45.8	4.2	2.3					
	11:15	0.685	0.012[d]	0.35	7.6	5.8	10.7	16.1	2.6	51.2	4.3	2.0	0.185	1616		0.077	Normal working.
X-1	12:40	1.12	0.007[d]	0.30	7.7	4.6	12.7	23.0	4.2	38.0	4.8						
	1:14	0.96	0.008[d]	0.34	7.0	2.8	10.8	22.5	3.8	45.4	4.8	3.2	0.138	1582		0.11	Normal working.
X-2	1:14	0.96	0.008[d]	0.34	7.0	2.8	10.8	22.5	3.8	45.4	4.8	3.2					
	2:00	0.85	0.009[d]	0.42	5.8	3.7	8.2	20.2	3.5	49.5	4.7	4.2	0.125	1602		0.16	Normal working.
X-3	2:00	0.85	0.009[d]	0.42	5.8	3.7	8.2	20.2	3.5	49.5	4.7	4.2					
	2:37	0.74	0.011[d]	0.46	6.0	4.1	8.4	18.3	3.4	52.1	4.7	3.7	0.126	1617		0.12	Normal working

[a] Determined by reduction with hydrogen. [b] Average for the entire period. [c] Estimated from pouring temperature. [d] Estimated from the relation (C)(FeO) = 0.0080. [e] Estimated from the notes on slag condition.

These data were obtained by drawing smooth curves through the experimental points. The mol fraction FeO, the temperature and the slag viscosity are averages over the entire period, as is the per cent. manganese in the metal. The slag analyses are shown to give the reader an idea of the type of slag and if the slag hanged considerably from beginning to end of the period two analyses are given as indicated.

The only serious difference between the calculated temperature and the tapping temperature is on heats *N* and *P*. From the appearance of these heats it is felt that the calculated temperatures are most certainly low and the observed temperatures too high, and for uniformity the results have been calculated from the calculated temperature instead of attempting to estimate the true temperature.

TABLE 2.—*Data for Calculation of Diffusion Coefficients*

Heat and Period		Weight Metal Lb.	Slag-metal Area, Sq. Ft.	$\frac{dc}{d\theta}$, Per Cent. per Min.	$\frac{dc}{d\theta}$, Lb. per Min.	FeO from Carbon, Elimination per Min., Lb. (1)	FeO at Start, Lb. (2)	FeO at End, Lb. (3)	FeO Increase, (3) − (2) = (4)	FeO Increase per Min., Lb. (5)	Total FeO Diffusing, Lb. per Min. (1) + (5)	FeO Actual, Average, Per Cent.	FeO Saturated, Average, Per Cent.	ΔFeO, Average, Per Cent.	H, Per Cent.	Average C, Per Cent.	Remarks
B-1	6:40–7:00	227,000	429	0.00720	16.35	97.8	37.6[b]	52.2[b]	14.6	0.7	98.5	0.020	0.210	0.190	1.16	0.41	Ore at 6:25.
B-2	7:00–7:15	227,000	429	0.00467	10.60	63.3	52.2[b]	65.8[b]	13.6	0.9	64.2	0.026	0.244	0.218	1.21	0.31	Normal working.
B-3	7:15–7:30	227,000	429	0.00327	7.22	44.4	65.8[b]	81.6[b]	15.8	1.1	45.5	0.033	0.254	0.221	1.30	0.25	Normal working.
B-4	7:40–8:00	227,000	429	0.00350	7.73	47.5	118.0[b]	213.0[b]	95.0	4.8	52.3	0.074	0.292	0.218	1.41	0.12	Normal working.
B-5	8:15–8:30	235,000	429	0.00274	6.45	38.5	103.2[b]	134.0[b]	30.8	2.0	40.5	0.050	0.238	0.188	1.32	0.16	8000 hot metal at 8:09.
B-6	8:30–9:00	235,000	429	0.00167	3.93	23.5	134.0[b]	209.0[b]	75.0	2.5	26.0	0.073	0.278	0.205	1.44	0.12	Normal working.
J	1:55–2:12	98,400	194	0.00453	4.47	26.7	38.0[b]	60.6[b]	22.6	1.3	28.0	0.049	0.277	0.228	1.12	0.17	After ore addition.
J	2:31–2:37	99,400	194	0.00500	4.93	29.5	72.5[b]	99.5[b]	27.0	4.7	34.2	0.085	0.314	0.229	1.16	0.095	During reboil after silicon addition.
K	9:18–9:27	94,750	192	0.00444	4.20	25.1	76.5[b]	128.0[b]	51.5	5.7	30.8	0.103	0.246	0.143	1.22	0.079	After spiegel addition.
K	9:30–9:35	95,750	193	0.00600	5.74	34.3	120.0	98.5	−21.5	−4.3	30.0	0.112	0.286	0.174	1.38	0.084	After cold pig addition.
N	2:03–2:22	97,650	194	0.00684	6.68	39.9	29.3	109.5	80.2	4.2	44.1	0.063	0.385	0.322	1.30	0.20	After ore addition
N	2:46–2:52	97,750	194	0.00490	4.79	28.6	118.5	145.0	26.5	4.4	33.0	0.134	0.345	0.211	1.36	0.066	During reboil after silicon addition.
P	5:24–5:39	102,350	196	0.00515	5.26	30.4	59.3	76.8	17.5	1.1	31.5	0.065	0.238	0.173	1.07	0.175	After ore addition.
P	5:56–6:04.5	102,450	196	0.00447	4.58	27.4	83.0	142.5	59.5	7.0	34.4	0.107	0.336	0.229	1.30	0.077	During reboil after silicon addition.
Q	11:11–11:51	197,190	341	0.00212	4.08	24.4	124.0	212.0	88.0	1.8	26.2	0.085	0.354	0.269	1.39	0.108	During reboil after silicon addition.
R	8:44–9:33	205,250	345	0.00282	5.79	34.6	32.8	59.5	26.7	0.5	35.1	0.022	0.184	0.162	0.94	0.243	Normal working.
R	10:02–10:16	205,500	345	0.00485	9.94	59.3	32.9	166.4	133.5	9.5	68.8	0.040	0.229	0.189	1.17	0.136	During reboil after silicon addition.
U	6:15–6:22	101,775	196	0.00615	6.25	37.3	62.0	86.4	24.4	3.6	40.9	0.072	0.435	0.363	1.43	0.080	During reboil after silicon addition.
V	9:25–9:43	196,720	341	0.00295	5.80	34.7	61.0	159.0	98.0	5.4	40.1	0.056	0.327	0.271	1.40	0.150	During reboil after silicon addition.
W	10:20–11:15	166,000	305	0.00455	7.55	45.3	14.9[b]	19.9[b]	5.0	0.1	45.4	0.010	0.272	0.262	1.45	0.81	Normal working.
X-1[a]	12:40– 1:14	166,000	305	0.00470	7.80	47.0					47.0	0.008	0.171	0.163	1.24	1.04	Normal working.
X-2[a]	1:14– 2:00	166,000	305	0.00239	3.96	23.8					23.8	0.009	0.171	0.162	1.34	0.91	Normal working.
X-3[a]	2:00– 2:37	166,000	305	0.00298	4.94	29.6					29.6	0.010	0.184	0.174	1.45	0.80	Normal working.

[a] Neglect FeO pick-up on heat *X*. [b] Estimated from the relation (c) (FeO) = 0.0080.

indicate that it was more viscous than the other heats, and though the following discussion will consider 0.30 as the correct value, it must be remembered that this is only an estimate, as is the value of 0.25 in. in heat *U*.

No measurements of metal viscosities are available, and the only data known to the writer are those of Thielmann and Wimmer[11] on cast

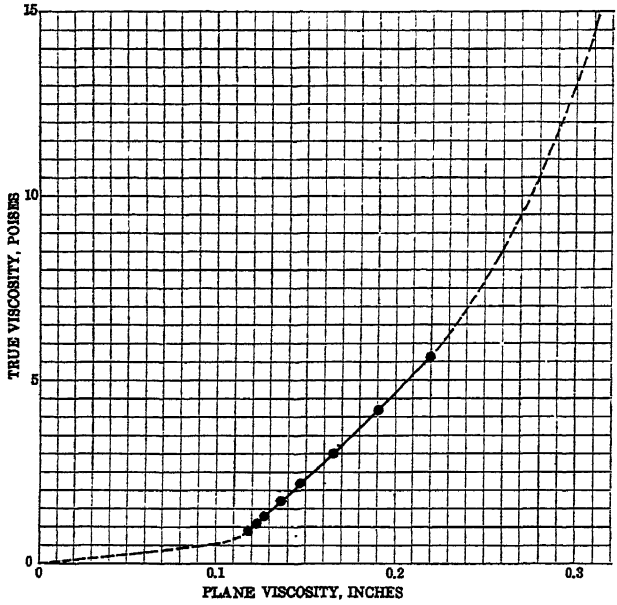


FIG. 1.—INCLINED PLANE VISCOSITY VS. TRUE VISCOSITY.

iron. Although extrapolation of their data is dangerous, nevertheless in the absence of other data they will be used. Their results, when extrapolated give the following (Table 3) for the viscosity of low-carbon steel:

TABLE 3.—*Extrapolation of Viscosity Data from Thielmann and Wimmer*

Temperature, Deg. C.	Viscosity, Poises
1500	0.0340
1525	0.0305
1550	0.0275
1575	0.0250
1600	0.0232
1625	0.0218
1650	0.0205

[11] A. Thielmann and A. Wimmer: Ueber die innere Reibung von flüssigem Roheisen. *Stahl und Eisen* (1927) **47**, 389.

Over-all Coefficients

Table 4 gives the results of the calculations on the over-all diffusion coefficients, K_s and K_m, the table being arranged in order of decreasing values of K_s.

The effect of slag viscosity on the coefficients is plainly seen, the coefficients decreasing with increasing slag viscosity. The exceptions to the general trend may be explained by a consideration of the conditions under "remarks." Until more exact measurements of slag viscosity are made it will be difficult to obtain the quantitative relationship between diffusion coefficient and slag viscosity, but the effect is so pronounced that the slag film is probably controlling in the diffusion process, with the metal film and the temperature coefficient of diffusion playing a secondary role.

Table 4.—*Values of Diffusion Coefficients, K_s and K_m*

Heat	K_s	K_m	Slag viscosity, Poises	Metal viscosity, Poises	Temperature, Deg. C.	Remarks
B-1	1.41	1.21	2.80	0.0255	1571	After violent ore boil.
R_r	1.24	1.06	1.65	0.0255	1572	Boil on bottom.
X-1	1.17	0.95	0.65	0.0238	1592	
N_r	1.10	0.81	0.90*	0.0233	1600	
P_r	1.00	0.77	0.50	0.0238	1591	
P_w	0.99	0.93	0.50*	0.0270	1555	
N_w	0.92	0.71	0.45	0.0240	1590	
J_r	0.89	0.77	0.90*	0.0255	1570	
W	0.83	0.57	0.40	0.0223	1616	
B-2	0.83	0.69	1.85	0.0250	1577	
U_r	0.83	0.58	7.50*	0.0226	1610	
X-3	0.82	0.57	0.90	0.0223	1617	
B-4	0.79	0.56	2.35	0.0227	1608	
J_w	0.71	0.63	7.50	0.0260	1565	Ore addition just before this period.
X-2	0.64	0.48	2.80	0.0230	1602	
B-3	0.62	0.48	4.20	0.0239	1590	
V_r	0.60	0.43	4.25	0.0230	1605	
R_w	0.59	0.63	0.90	0.0293	1534	Note low temperature.
B-6	0.43	0.30	3.30	0.0225	1611	
Q_r	0.40	0.29	13.00*	0.0230	1604	
K (spiegel)	1.37	1.12	2.35	0.0243	1585	
K (pig)	1.23	0.91	1.20	0.0232	1602	
B-5	0.66	0.50	5.10	0.0236	1594	

* Estimated from appearance of slag—not measured.

The effect of low metal temperature is seen in period R_w, where the coefficient was low even though the slag was very fluid. The temperature during this period was much lower than at any other period given, and the low coefficient is probably due to both high metal viscosity and low diffusivity of FeO at this low temperature.

Using $K_m = 0.80$ and $K_s = 0.98$ and transposing from the units of this paper to those of Lewis and Whitman [multiply K_m by 418 and K_s by 89 by changing from lb. per min. per sq. ft. per unit concentration difference (mol. fraction for slag and weight per cent. for metal), to g. per hv. per sq. cm. per unit concentration difference (g. per c.c. of solution)], we obtain $K_m = 334$ and $K_s = 87$. The constants are high compared to those found by Lewis and Whitman and others, and indicate that the temperature coefficient of diffusion is even higher than estimated on page 289, especially in view of the high viscosity of open-hearth slags when compared with water.

The three periods given at the bottom of the table, periods *K* (spiegel), *K* (pig), and *B*-5, a small hot metal addition, show coefficients higher than would be expected from the slag viscosities reported. This is undoubtedly due to the fact that *carbon* was added to the bath in these heats, and the immediate reaction plus the agitation resulting therefrom increased the rate of diffusion of FeO from slag to metal.

An interesting point in this connection is that there is a definite relationship between the coefficient of diffusion of material through a gas film and the coefficient of heat transfer through the same film.[12] It is highly probable that the same condition holds true in liquid films, and the increase in temperature of the bath on the addition of spiegel or pig iron is well known, and may be correlated with the high diffusion coefficients noted above—that is, heat transfer and diffusion increase simultaneously.

It should be particularly noted in studying these data that a wide range of conditions have been covered. The variation in conditions follows:

Size of furnace, tons	40	to 100
Slag-metal area, sq. ft.	195	to 429
Carbon content of bath, per cent	0.06	to 1.12
Slag viscosity, poises	0.40	to 13.00
Metal temperature, ° C	1534	to 1617
Iron oxide content of slag, mol fraction	0.125	to 0.305
Iron oxide content of slag, per cent	10	to 27

With these wide variations the results of the calculations of the diffusion coefficients may be considered extremely satisfactory.

[12] W. K. Lewis: The Evaporation of a Liquid into a Gas. *Mech. Eng.* (1922) **44**, 445.

Film Coefficients

As mentioned previously, the conductivities of the liquid films may be considered proportional to the ⅔ power of the ratio of density to viscosity of the liquids under consideration. The normal creamy open-hearth slag has a plane viscosity of 0.10 to 0.12 in., equal to a true viscosity of 0.65 to 0.90 poise. The density of $CaO.SiO_2$ is 2.89 and the other components in the slag increase this value to about 3.25. From Table 3 the viscosity of steel is approximately 0.023 poise at 1600° C., and its density about 7. The relative film conductivities for slag and metal would therefore be:

Slag $\left(\frac{3.25}{0.80}\right)^{⅔} = 2.53$, and for steel $\left(\frac{7.0}{0.023}\right)^{⅔} = 45.7$. In other words, the metal film is much more conductive than the slag film.

Using heats P_w, N_r, J_r, P_r, and N_w (periods when conditions are fairly comparable), the average value of $K_m = 0.80$ and of $K_s = 0.98$. The average value of H (the solubility relationship) is 1.23 for these periods. Now, if we assume that the film conductivities have the relative values given under the conditions specified above, $k_s = \frac{k_m}{18.1}$, the relation $K_m = \frac{k_m k_s}{H k_m + k_s}$ becomes

$$k_m = K_m\left(H + \frac{1}{18.1}\right)(18.1) = 0.80(1.23 + 0.055)(18.1) =$$

$$18.6 \text{ and } k_s = \frac{18.6}{18.1} = 1.03.$$

It will be noted that the slag film coefficient, $k_s = 1.03$, is almost identical with the over-all coefficient based on slag concentrations, $K_s = 0.98$, showing that the slag film is the controlling factor, as indicated by the data of Table 4.

To visualize conditions at the slag-metal interface, consider the following conditions:

Concentration of FeO in the metal = 0.100 per cent. (with 0.08 per cent. C).

Concentration of FeO in the slag = 25 per cent. = 0.270 mol fraction.

Temperature = 1580° C., whence $H = 1.23$.

Saturation value of FeO in the metal = (0.270) (1.23) = 0.332 per cent.

Let $K_m = 0.80$; $k_m = 18.6$ and $k_s = 1.03$ as indicated above.

Now from equation (3) $\frac{d\text{FeO}}{A d\theta} = K_m(\text{FeO}_{\text{slag}} - \text{FeO}_{\text{metal}}) = 0.80(0.332 - 0.100) = 0.186.$

Also, from equation (1)

$$\frac{d\text{FeO}}{A d\theta} = k_s(\text{FeO}_{\text{slag}} - \text{FeO}_{\text{interface}}) = k_m(\text{FeO}_{\text{interface}} - \text{FeO}_{\text{metal}}).$$

The concentration at the slag side of the interface will be

$$FeO_{interface} = FeO_{slag} - \frac{\frac{dFeO}{A d\theta}}{k_s}$$

Whence $FeO_{interface} = 0.270 - \frac{0.186}{1.03} = 0.089$ mol fraction FeO. The slag and metal are in equilibrium at the interface, whence the concentration at the metal side of the interface is $\left(\text{from the relation } H = \frac{FeO_{metal}}{FeO_{slag}}\right)$, $H(FeO_{slag}) = 1.23(0.089) = 0.110$ per cent., and the concentration in the metal itself is 0.100 per cent. These conditions are shown in Fig. 2, and illustrate the importance of slag control in any steelmaking process, the process of diffusion being controlled almost entirely by the slag film.

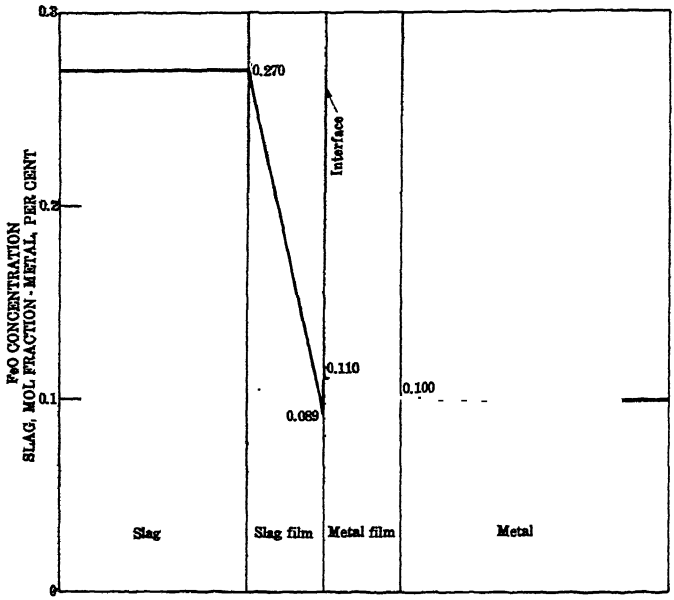


FIG. 2.— DIAGRAMMATIC REPRESENTATION OF CONDITIONS AT SLAG-METAL INTERFACE.

APPLICATIONS OF THEORY

The importance of being able to control the rate of diffusion of FeO from slag to metal may be illustrated by the following examples:

1. In making rimming steel it is of the utmost importance that the metal shall give off gas at a definite rate during solidification in the ingot mold. This gas rate is a function of how fast gas is being formed in the furnace and this in turn depends on the rate of diffusion of iron oxide from slag to metal. Once the film coefficients are known and viscosities of various types of slag are determined, the rate of oxidation of

the metal will be under much closer control than is possible at the present time.

2. After steel is deoxidized in the furnace it is customary to allow the heat to remain in the furnace until the steel has had a chance to "clean itself"—that is to say, allow the nonmetallic matter to rise into the slag. The rate at which this nonmetallic matter enters the slag is primarily determined by the size of the particles and this in turn is controlled to a considerable extent by the amount of fluxing with FeO which is diffusing from the slag into the metal. To obtain the proper amount of fluxing and not oxidize the metal so that the work of deoxidation is nullified is a question of slag control and extreme skill of the operator in judging physical conditions in the bath. The same condition holds for ladle slags. The last few ingots of many heats of steel, both rimmed and killed, are of inferior quality, due either to nonmetallic matter which has not been eliminated from the steel or to too rapid diffusion of FeO into the metal during teeming, with consequent increase in nonmetallic matter on killed steels and too heavy a gas evolution on rimmed steels.

3. There has been considerable discussion during recent years on the question of double slags in steelmaking processes. An important point in this connection is that if a deoxidizing slag is put on an oxidized bath, care must be taken that the slag is fluid, as the deoxidation of the metal will be largely controlled by the rate at which FeO can penetrate the slag film.

DISCUSSION

C. H. HERTY, JR.—Recent work which we have completed at Pittsburgh has shown that certain of the data in this paper are not only slightly incorrect, but in some instances entirely incorrect. In the table on page 291, column 4 gives the FeO content of the metal. This was generally determined by reduction of the sample with hydrogen and weighing the water formed. Sometimes, where it was not possible to make this determination, the amount of FeO was calculated from the relation of (C)(FeO) which is equal to 0.0080. We have found that this figure is incorrect and that this is reflected on all of the constants calculated where that particular figure is used.

G. B. WATERHOUSE, Cambridge, Mass.—Is it correct to ask what the new constant is?

C. H. HERTY, JR.—The new work indicates that there is not a new constant that can be directly applied to open-hearth work. That is, the constant is mixed up with other things, such as slag composition, which is a primary factor. We will not try to give any values of m in this work, and we will have to wait just a little while until we determine the exact relation between the slag composition, the metal composition and the amount of carbon in the metal before we can predict the FeO content of the metal.

On the other hand, the values are so different from those given in the paper that I will not try to point out any particular diffusion constant, but I will simply derive the diffusion constant, and the effects that you can expect from that on open-

hearth operation. So please remember that the values for FeO in the metal are incorrect.

A. B. KINZEL, New York, N. Y.—In attacking the problem of the open hearth from the theoretical standpoint, it is always well to go back to fundamentals. We have been interested in the problem at the Union Carbon and Carbide Research Laboratories from some years now, and as the result of much discussion and thought an equation was evolved by Mr. Feild, previously mentioned by Dr. Herty in his paper, and published in Iron and Steel Technology in 1928.[13]

That started out with the basic assumption that the operation in the open hearth is not a static system but is distinctly dynamic. Many things are happening. Changes are going on all the time, and one change affects the other. Dr. Herty pointed out in his discussion three major phases that have to be considered. Change in viscosity of the slag is one action that is going on all of the time. The viscosity of the slag is constant for a short period, but it does change. The oxide content of the slag is another. For any given short period it is fairly constant. Bath conditions, that is the rate at which the carbon or other elements which oxidize readily are removing oxygen from the bath, are the third consideration.

There have been set up three distinct rate equations involving all of the factors mentioned. These have been treated as simultaneous equations, acting at the same time and affecting each other, and from them has been evolved one equation.

Nothing that Dr. Herty has said here has contradicted or caused us to deviate one bit from the basic assumptions and general views reflected in that formula; in fact, if he follows his argument, as he has started it here, to its logical conclusion, I do not see how he can help arriving at the same equation.

Another factor is the equilibrium of the iron oxide and carbon in the bath. That was known as m and has been referred to several times, and m at equilibrium was at that time unknown. Perhaps it is still unknown, but it entered into the problem. We believe now that it is so low that we do not have to take it into account to the extent that we had supposed.

What we need is more quantitative data. We theorize. We know approximately what happens. It has long been assumed that increase in viscosity changes the rate of oxide diffusion. We know that the degree of oxidation of slag has an effect—the question is, how much? We want to get it down to quantitative terms, and as long as we talk, not exactly generalities, but qualitatively, we are almost as far from being able to thoroughly understand the process, or even from our most pleasant dream of actually being able to assist in the operation of the open hearth, as we were when we first set down the fundamental principles and appreciated their significance.

Much credit is due Dr. Herty for the way he has presented the paper and brought out forcefully the factors that are involved, and I hope that his future work at the Bureau will tend toward quantitative work on this subject, so that in the not too distant future—that is, before most of us die—we will have something like quantitative approximation of what is going on.

With regard to this matter of m, Dr. Herty said that if we knew m we would know the condition of the bath. True, to get m we have to measure the oxide content. After all, that is what we are interested in, so why complicate the situation by giving the condition of the bath as the function of m? Why not say that it is the function of the oxygen content, because if we say m we have to take into consideration the

---

[13] A. L. Feild: Rate of Carbon Elimination and Degree of Oxidation of the Metal Bath in Basic Open-hearth Practice. Iron and Steel Technology in 1928, A. I. M. E., 114.

carbon content as well? The idea is correct, but I think it is taking a theoretical step that is unnecessary.

This matter of m needs further consideration, and I discuss it in detail in the following paper.[14] m was originally defined as the product of iron oxide and carbon, and conditions may be such that discrepancies in the value of m may arise. It must be remembered, in connection with the definition of m, that until quite recently m was supposed to be the equilibrium condition. That is one thing. The way Dr. Herty is using it now, it is the product of iron oxide and carbon and it certainly is not m at equilibrium, which is a very definite thing. The new m depends on rates, slag viscosity and all of the other factors that come into the open hearth.

H. STYRI, Philadelphia, Pa.—I would like to point out another phase in this reaction which has been overlooked in the previous papers and, I believe, in this paper. The furnace atmosphere is over the slag which is on top of the surface of a steel bath. During the carbon drop, which may be represented by a straight line or some other line, the iron oxide content of the slag can be fairly constant over a considerable length of time. What causes that? I figure this way: the oxygen from the atmosphere diffuses into the slag. Iron vapor will diffuse in the slag, and the two combine to iron oxide. We do not need to add iron oxide in the form of iron ore or scale in order to keep the iron oxide content in the slag constant. It is easy to check that by changing the condition of the atmosphere. If that is the case, then, of course, the thickness of the slag—and I mean the dimension, not the viscosity—has a great influence on the rate at which carbon drops; so when such studies are made, the thickness of the slag should certainly be calculated, or measured to see what influence that has. I believe that the thicker the slag, the slower the rate of carbon drop; it may even be nearly proportional to the thickness.

Further on we may say, as Dr. Herty says, that at the interface the iron oxide diffuses into the steel. That means that that iron oxide goes down at a certain rate along this interface, and, of course, the concentration of oxygen in the steel bath must be the highest near the top, because from the bottom the carbon atoms diffuse upward; they will meet and combine to carbon monoxide, and will rise in the form of gas bubbles and their volume will be larger near the top. Consequently, if different samples of the steel are taken a difference in concentration will be found near the top and further down in the bath.

Such measurements were made in Germany three or four years ago by Dr. H. Neuhauss.[15] This must be considered when the rate of diffusion is taken into account.

Dr. Herty's statement will not contradict Mr. Feild's equation No. 3, which is correct but is not new (Piérard, in France, had that same equation) but it certainly does not prove that his equation No. 7 is correct, and that is a very poor mathematical contribution to metallurgy.

C. H. HERTY, JR.—In regard to Mr. Kinzel's remarks about Feild's equation, I never questioned Feild on the form of the equation, but there were two things that I did think were in error in his equation. One was the constants, which we know now are far from right.

In regard to Dr. Styri's remarks, I think I said in presenting my paper that the iron oxide in the furnace would come from oxidation by the furnace gases. Whether it is metallic iron vapor diffusing up and oxygen diffusing down, or whether it is

---

[14] A. B. Kinzel and J. J. Egan: Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron. See p. 304.

[15] F. Körber, F. Wever and H. Neuhauss: Ueber die Verwendung des Hochfrequenz-Induktionsofens für die Edelstahlerzeugung. *Stahl u. Eisen.* (1926) **46**, 1648.

FeO oxidizing at the slag metal surface being carried down by diffusion, or convection, I do not know. Possibly it is both. Nevertheless, if you are studying this, and have a slag analysis, you need not worry, providing you know what the slag analysis is at the time you are interested in it.

I believe unquestionably that the slag thickness will slow down the furnace, but I have always believed that it was a question more of getting heat into the bath than of anything else; that the thicker the slag, the slower the furnace works on account of resistance to heat flow from the gas into the metal, rather than the diffusion of iron oxide from the surface below.

Whether slags ever get so thick that convection currents will not bring the upper part of the slag into contact with the metal, I do not know. That would be a subject for considerable experimental work, and on the question of this gradient of FeO from the slag metal surface into the metal, I would like to ask Dr. Styri how far down that gradient existed, and how different was the value, and how the oxygen measurements were made.

H. STYRI.—That information is given in Dr. Neuhauss' paper.[16] I think a difference found as far as 40 cm., say about a foot or more, from the surface.

C. H. HERTY, JR.—In the first place, I think the methods we have been using for analyzing oxygen are wrong. To take a test piece out of a furnace, pour it into a mold and analyze for oxygen, as we have been doing for two or three years, is an entirely incorrect procedure. That is why we get values for m of 0.0080 and 0.0016. It seems to me that with a normal boil in the furnace, there is enough agitation in the metal bath to keep the upper part at about the same composition as the lower. I grant you that there may be a skin of metal underneath which would be entirely different in composition, but if you go 40 cm., or 1 ft. down in the bath it is difficult to comprehend.

H. STYRI.—I have not read the paper for a year and I may have forgotten.

A. B. KINZEL.—Dr. Styri mentioned the matter of Piérard's equation No. 3, so I would like to point out that the three basic equations, on which equation No. 7, which is in dispute, is based, are not really at all new in themselves. They are three old equations taken bodily out of the field of physical chemistry, and are familiar to and generally used by physical chemists. It is a question of pure logic. The new part of it is putting those three equations together, solving them simultaneously and getting one equation out of them, to get the interrelated effect, and I might add that there is a disagreement as to the value of equation No. 7, and not all metallurgists agree with Dr. Styri that it is a poor mathematical contribution to metallurgy.

G. B. WATERHOUSE.—Dr. Kinzel spoke of the assumption that thickness of the slag helped in refining the bath. That has been practiced for a great many years. One of the first recollections I have is of a well known open-hearth man. He has had no scientific training, but is employed by one of the makers of deoxidizing agents. The first thing that man would do when the heat was pretty well shaped up would be to thicken up the slag and let it remain quiet for about 30 min., then add the deoxidizer.

G. A. DORNIN, Baltimore, Md.—I think this discussion of Dr. Herty's paper makes it quite clear why rimmed steel is one of the hardest kinds of steel to make well, for the only thing that can be done in the final shaping up of the bath is the control of the viscosity of the slag.

---

[16] F. Körber, F. Wever and H. Neuhauss: *Op. cit.*

Steel is made to rim so that the shrinkage volume of the steel will not be concentrated but dispersed all through the body of the ingot with only the ingot skin sound, the core inside the skin being highly segregated as well. To rim properly there must be just the right amount of gas evolution, if too much there is foaming, if too little there are surface blowholes.

Deoxidized steel is distinctly different. Here the shrinkage volume of the steel is concentrated in a single pipe cavity if the fundamental laws of solidification are followed and this piped portion can be made to occur in a very small portion of the top of the ingot where it can be cropped with little loss, leaving the remainder sound.

In deoxidizing, the slag viscosity is first increased and the deoxidation begun, but when this has done what it can do the deoxidation process is then carried on by adding deoxidizers such as silicon, manganese, and aluminum and these reduce FeO leaving their oxides in its place.

In discussing a recent paper by myself,[17] Dr. Gillett called the making of the products of deoxidation fusible a hair trigger operation and as the basic open-hearth process is operated today, I agree with him. I do not think, however, that the basic open hearth is today operated along sound metallurgical principles. If it were and I think that it can be and in the near future will be, and if we can have some means to tell us just how much FeO there is in the bath and if from that time on no more FeO will diffuse from slag to bath then when deoxidizers are added, we should be able to form the products of deoxidation in the proper proportions so that there will be self-fluxing and thereby colloidal action and clean steel. It does not seem to me that under these conditions it is a hair trigger operation at all and I believe that the research work of Dr. Herty will soon give us the data we need.

---

[17] G. A. Dornin: The Slags Produced in Steel Making—Their Effect on the Product and on the Process Itself. *Trans.*, A. S. S. T. (1929) **16.**

Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron

By A. B. Kinzel* and J. J. Egan,* New York, N. Y.

(Cleveland Meeting, September, 1929)

Much work has been done recently in an attempt to analyze the physicochemical mechanism involved in the production of steel by the open-hearth process. This has resulted in reducing the process to a series of interrelated phenomena obeying the usual laws of mass action and diffusion. Of these, the reaction of the iron oxide and carbon in the molten steel is of most interest from a technical point of view as it constitutes the main action in the usual steelmaking processes.

A. L. Feild[1] has formulated a basic differential equation expressing the open-hearth reactions and Herty has done considerable experimental work on the determination of a number of constants involved in the basic open-hearth reaction. In considering the application of the law of mass action to the reaction $FeO + C \rightleftarrows CO + Fe$, the iron will be taken as constant, as is the case in the open hearth and the carbon monoxide pressure will be assumed constant at one atmosphere. From this $xy = m$ at equilibrium, where x is the percentage weight of carbon, y percentage weight of iron oxide and m the weight-concentration equilibrium constant. While it is customary for physical chemists to express equilibrium constants in terms of molar concentrations, the constant is here expressed as the product of the percentage-weight concentrations for ease of comparison with the constants quoted by Herty and by Feild, and for more ready applicability to the open-hearth reactions. Herty and his associates have attempted to calculate the value of this constant from data on open-hearth heats. So many variables affect these results that an adequate calculation presents very great difficulties. A value of 4×10^{-2} was first arrived at, but this was later changed to 1.6×10^{-2}. Feild, in order to illustrate the operation of the differential equation of the open hearth, has assumed a value considerably lower than Herty's, namely, 1.0×10^{-2}, the largest value consistent with certain theoretical

* Union Carbide and Carbon Research Laboratories, Inc.

[1] A. L. Feild: Rate of Carbon Elimination and Degree of Oxidation of the Metal Bath in Basic Open-hearth Practice. Iron and Steel Technology in 1928, A. I. M. E. (1928) 114.

considerations. Subsequently, Herty had assumed a still lower value, namely 0.8×10^{-2}.

In considering experimental methods for determining this constant the authors decided that a method of attack originally suggested by A. L. Feild held decided promise. Feild believed that it would be possible to obtain the equilibrium constant experimentally by starting with iron containing no oxygen and carbon, and building up to equilibrium value by holding in a suitable atmosphere. In line with this suggestion, the following method was adopted.

Determination of Equilibrium Constant

The general plan by which determination of the equilibrium product of iron oxide and carbon has been attempted consists essentially in starting with iron having negligible carbon and oxygen contents and holding at a constant temperature in an atmosphere of carbon monoxide at constant pressure, said pressure preferably one atmosphere. For check purposes irons containing high carbon and high oxygen respectively are also used. After holding until equilibrium conditions are deemed to be established, the molten metal is chilled as rapidly as possible and the ingot analyzed for carbon and oxygen. The only assumptions necessary in carrying out this plan are that equilibrium has been reached and that the change in concentration of oxygen and carbon on cooling is negligible. It is believed that the assumptions are justified by the data given later.

Materials and Apparatus

Electrolytic iron was used throughout the experiments. This was melted in vacuo in order to extract hydrogen and possibly other gases before being subjected to the experimental conditions, in certain instances. Chemically pure magnetic iron oxide was used to make up a high-oxygen bath in one run and activated charcoal was used for carburizing in preparing material for the high-carbon bath used in another run. The metal in each case was melted in a small magnesite crucible. This was prepared by ramming moist, iron-free, electrically fused magnesia in a mold with a very small amount of calcined magnesia and firing at 2000° C. for 2 hours.

Carbon monoxide was prepared by dropping c.p. formic acid into concentrated c.p. sulfuric acid. The gas was then passed through sulfuric acid and ascarite as shown in Fig. 1. Gravimetric analysis of samples of the gas showed absence of hydrogen and hydrocarbons. A three-way stopcock followed the generating train permitting it to be thoroughly flushed with carbon monoxide up to the furnace connection.

The experiment proper was carried out in a Sarbey furnace (Fig. 2). This is essentially an electrical resistor furnace operating over a Torri-

cellian vacuum or in any suitable atmosphere. The resistor consists of a molybdenum cylinder made up of two thin sheets clamped at each end. The cylinder is suspended from the upper clamp which fastens to the water-cooled conductor. The lower ends of the sheets are clamped to a sliding sleeve which makes contact in mercury to complete the circuit.[2] The furnace proper is housed in a steel cylinder jacket, the walls of which are water-cooled. This jacket extends down to a bath of mercury. When the vacuum is drawn in the jacket, the mercury rises to the barometric height. The three-way stopcock previously referred to allows the carbon monoxide generator to be connected with the furnace without first break-

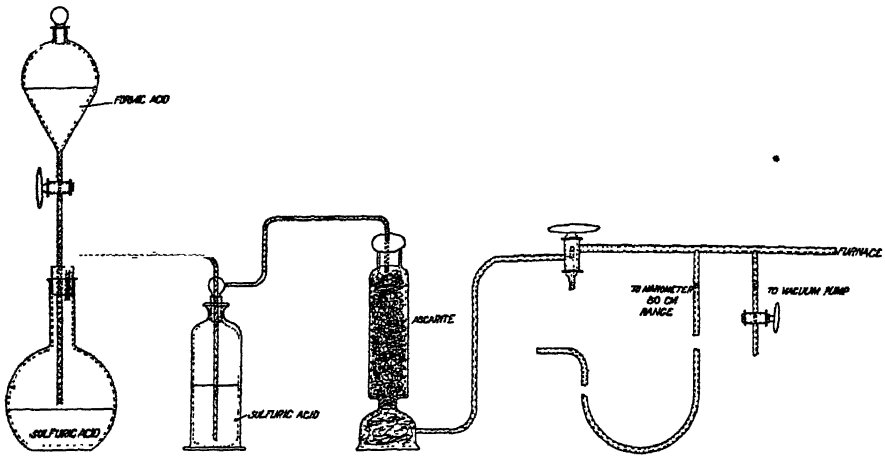


FIG. 1.—CARBON MONOXIDE GENERATOR AND TRAIN.

ing the vacuum. The connecting line also carries a mercury manometer of 80 cm. range. A second outlet with a stopcock just above the point of maximum barometric height allows circulation of the carbon monoxide if desired. A sighting tube with special plate glass cover is fitted to the cylinder.

An optical pyrometer was sighted on the metal in the crucible through the plate glass cover. The pyrometer was calibrated against a standard lamp certified by the Bureau of Standards.

PROCEDURE

Clippings from electrolytic iron sheets were placed in the crucible (about 50 g. were used) and melted in the Torricellian vacuum. Simultaneously the carbon monoxide generator was started by dropping the formic acid on the sulfuric acid and the carbon monoxide passed through the train and out to the open air. The melt was taken to a temperature

[2] For further description of the Sarbey furnace see Iron and Steel Technology in 1928, A. I. M. E. (1928) 303.

higher than that at which it was planned to run and then dropped back to the temperature in question which was 1550° C. This procedure was varied by passing the gas into the furnace as the temperature was rising but the results were not affected.

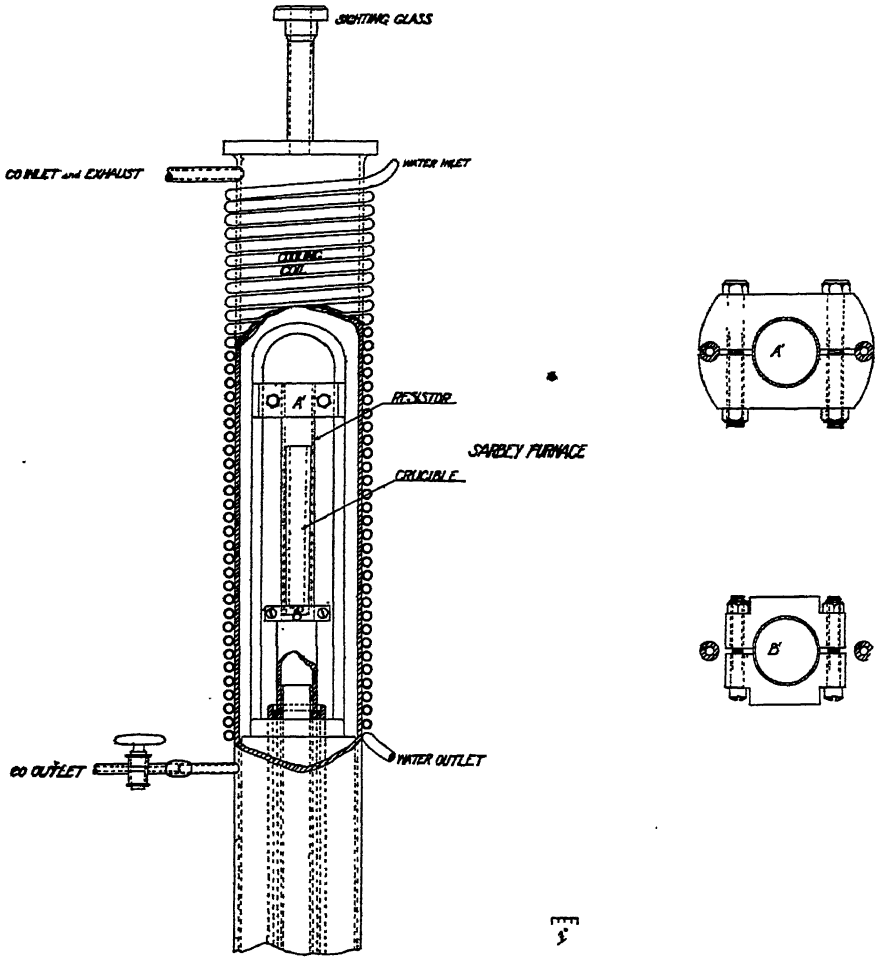


FIG. 2.—THE SARBEY FURNACE.
Scale refers only to furnace. *A'* and *B'* are approximately ¼ actual size.

The temperature of the furnace was controlled by means of rheostats. During the equilibrium period the temperature was held within 5°, although an occasional departure of 10° occurred, and for a period of at least 15 min. before cooling the temperature was carefully maintained within 3°. When the metal was brought to 1550° C. and the carbon monoxide train had been thoroughly flushed out, the stopcocks were turned allowing carbon monoxide gas to pass into the Sarbey furnace

and cutting the vacuum pump out of the system. In runs 1, 2 and 3, the carbon monoxide was passed into the furnace until a pressure of one atmosphere existed. The furnace was then sealed. As the gas heated up, the excess pressure caused it to bubble out from under the mercury seal as this was only a few millimeters deep. The pressure was thus automatically maintained at a trifle more than one atmosphere throughout the experiment. Variations in barometric pressure on the days on which these runs were made were not sufficient to warrant consideration. In the first runs the bubbling stopped and the manometer indicated constant pressure at the end of half an hour. (The constant pressure indicates that equilibrium has been established.) The temperature was then held constant for 2 hr. and the current turned off with resultant rapid cooling.

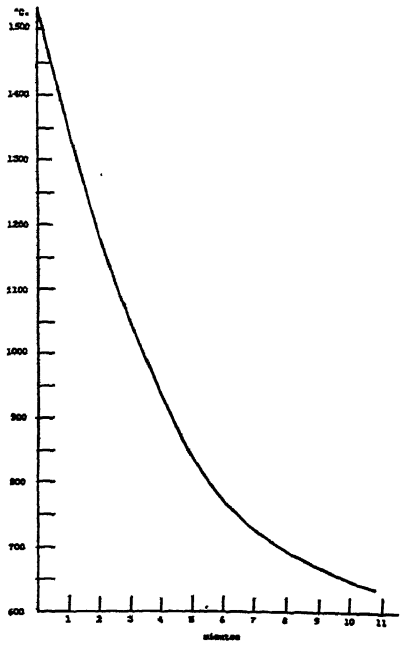


FIG. 3.—RATE OF COOLING OF ELECTROLYTIC IRON IN SARBEY FURNACE WITHOUT RADIATION SCREEN.

The curve in Fig. 3, taken on one of the melts, shows the very rapid rate of cooling obtained with this apparatus. This seems to justify the assumption that the material as obtained in the solid ingot has substantially the amounts of carbon and oxygen corresponding to equilibrium at the temperature used. Runs 1 and 2 were made with a charge of electrolytic iron and run 3 was made with a charge of carburized electrolytic iron running 1.67 per cent. carbon. In run 4 electrolytic iron was used but in this case instead of maintaining one atmosphere in the furnace by means of the mercury seal, carbon monoxide was passed continuously through the furnace throughout the holding period at approximately 25 c.c. per min. In run 5 the charge was made to correspond to 0.1 per cent. added oxygen. This run was held for 4 instead of 2 hr., the carbon monoxide being passed continuously.

After cooling, the ingots were carefully cleaned and analyzed. Oxygen analysis was made by the complete fusion method. The carbon was run in the usual combustion furnace. A large sample was used and several determinations were made. The results of both oxygen and carbon analyses are given with two significant figures although no claim is made for the accuracy of the second figure.

Results

The data including the calculated results are shown in Table 1.

Table 1.—*Experimental Data in Determination of Equilibrium Product of Iron Oxide and Carbon*

Run No.	Temperature, Deg. C.	Holding Time, Min.	Charge			Ingot			m	Remarks
			Material	C, Per Cent.	O, Per Cent.	C, Per Cent.	O, Per Cent.	FeO, Per Cent.		
1	1550	40	Electrolytic Iron			0.028	0.0041	0.018	5×10^{-4}	Sealed furnace.
2	1550	140	Electrolytic Iron			0.035	0.0032	0.014	5×10^{-4}	Sealed furnace.
3	1550	110	Electrolytic Iron Carburized	1.67		0.030	0.0037	0.017	5×10^{-4}	Sealed furnace.
5	1550	110	Electrolytic Iron			0.021	0.0048	0.022	5×10^{-4}	CO continuous.
6	1550	210	Electrolytic Iron and Iron Oxide		0.11	0.03	0.0042	0.019	5×10^{-4}	CO continuous.
7	1550	240	Electrolytic Iron			0.027	0.0051	0.023	6×10^{-4}	CO continuous.

Discussion

The results are particularly surprising in that they give a value for m, the carbon-iron oxide product, of 5×10^{-4}. This is considerably lower than has been hitherto supposed. The results, however, show a remarkable consistency and independence of initial concentrations. It is particularly surprising that such slight carburization of the melt takes place in the presence of carbon monoxide and that in one case (run 3) decarburization has occurred. The mechanism of this is probably to be found in the CO-CO_2 equilibrium with deposition of carbon on the cold walls of the container. In the instance in question considerable carbon was noted. The values obtained with runs of varying times indicate that sufficient length of time was given for equilibrium to be established. Moreover, the values on the runs with sealed furnace and with carbon monoxide passing through indicate that the composition of the gas in the sealed furnace experiments does not change materially during the run.

Sufficient work has been done to indicate that the order of magnitude of the equilibrium constant does not change with the temperature within the limits of usual steelmaking practice.

After sufficient work had been done to establish the equilibrium constant to our own satisfaction, the data were discussed with Herty. There was a lack of agreement between our values and those obtained by Herty from the open hearth. Moreover, the results did not agree with those of his early work of a similar nature. At the suggestion of Herty, a run was made in which a carbon ring was placed on top of the crucible so that the gases in contact with the metal were practically in equilibrium with solid carbon. The results were not affected. Further work was

then carried out to see the type of result that could be obtained with other equipment. Carbon monoxide was passed through a quartz tube over molten steel in an enclosed induction furnace. A large temperature difference existed between the ends of the quartz tube and heavy deposition of carbon took place. In addition, the carbon content of the bath was appreciably raised. This was undoubtedly due to the carrying of solid carbon particles to the bath surface. Our general experience indicates that solid carbon will carburize a bath of molten iron although it is evident from the equilibrium data that carbon monoxide gas will not carburize such a bath.

It is not the particular purpose of the authors to discuss the significance of the value of the equilibrium constant given here. It is apparent that if the value is as low as shown, current ideas on the mechanism of open-hearth reactions must be modified. Indeed, this modification has already begun. The essential conclusions of this report were disclosed at the Round Table Discussion of the Committee on the Physical Chemistry of the Open Hearth[3] and new explanations of the mechanism in the open hearth were advanced. The authors have always believed that the basic equation of Feild takes into account, quantitatively, the major elements of the open-hearth reaction. As soon as the new value for m was established, they realized, together with Feild, that if the new value for m was put in the Feild equation, it would necessitate changes in the assumed values of some of the other constants. It was obviously probable that the rate constant of the reaction or the effective CO pressure, or both, were of a different order of magnitude than previously assumed. As a result of this low value for the equilibrium constant, workers in the field of physical chemistry of the open hearth are now directing their attention to these phases.

Conclusions

1. The method of obtaining the iron oxide-carbon equilibrium constant used here gives consistent results.

2. The data indicate that 5×10^{-4} is the value of m at 1550° C. and one atmosphere pressure.

Acknowledgments

The authors wish to express their appreciation of the stimulating interest shown by F. M. Becket, President, and J. H. Critchett, Vice President, of the Union Carbide and Carbon Research Laboratories, Inc. They also wish to thank their colleagues at the Laboratory for helpful discussion and general assistance, and particularly to mention the work done by H. Willis and C. Kluge.

---

[3] See p. 233.

DISCUSSION

J. M. GAINES, JR., Cambridge, Mass. (written discussion).—Perhaps no experimental work of a metallurgical character has, in recent years, proved so thought-provoking as that described in the present paper. Not only in its bearing on the theorectical aspects of the problem, but also because of the implications of this theory when applied to practice, is the research of Messrs. Kinzel and Egan an extremely important contribution.

There are three possible reactions which may take place in the system under consideration:

$$CO + Fe = C + FeO \quad (1)$$

$$2CO = C + CO_2 \quad (2)$$

$$CO\ (gas) = CO\ (in\ solution). \quad (3)$$

No data are available on the solubility of CO in iron, save for the statement of Sieverts[4] that CO does not dissolve in any metal. For this reason, reaction 3 may be left out of consideration. It is apparent from the data that reactions 1 and 2 have both taken place, for if 1 alone were involved, the iron would contain carbon and oxygen in molecular proportions. Actually, the amount of carbon is five to 10 times that of oxygen.

The equilibrium actually measured therefore is that of iron containing carbon and iron oxide in contact with a mixture of CO and CO_2. Since the system is of three components in two phases, and since both temperature and pressure are fixed, the composition of one phase is fixed if that of the other is known.

An estimate of the gas composition in the runs in the sealed furnace can be made from the analysis of the metal phase and the dimensions of the apparatus. Assuming that the excess of carbon over oxygen in the metal is due to formation of CO_2 by reaction 2, and that the total gas space is about 6 liters, the average concentration of CO_2 will be about 0.6 per cent. (It is necessary also to assume that the average temperature in the gas space is 100° C.)

From thermodynamic data it is possible to calculate for the above gas concentration what should be the equilibrium concentrations of C and FeO in the metal. By subtraction of reaction 2 from 1 we have

$$FeO + CO = Fe + CO_2 \quad (4)$$

for which Garran[5] gives the following data:

$$K = \frac{(CO_2)}{(FeO)(CO)} = 0.25 \text{ at } 1550° \text{ C.}$$

It is assumed that changes in the specific heats of iron and FeO on fusion will cause negligible error and that the activity of pure FeO (or of FeO in a saturated solution in Fe) is unity, and is proportional to the concentration in dilute solutions. These assumptions apply also to dissolved carbon.

Similarly, for reaction 2 Lewis and Randall[6] give data by which the equilibrium constant may be calculated. Hence,

$$K = \frac{(CO_2)\,(C)}{(CO)^2} = 4.46 \times 10^{-5} \text{ at } 1550° \text{ C.}$$

---

[4] A., Sieverts: Absorption of Gases by Metals. *Ztsch. für Metallkunde* (1929) **21**, 37.

[5] R. R. Garran: Equilibrium in the System Iron, Oxygen, Carbon, *Trans.* Faraday Soc. (1928) **24**, 201.

[6] G. N. Lewis, and M. Randall: Thermodynamics, 574. McGraw-Hill Book Co., New York, 1923.

For a gas phase containing 0.6 per cent. CO_2 and 99.4 per cent. CO, the metal should contain 0.024 per cent. FeO and 0.041 per cent. carbon.

It is of interest that m in this case is 10×10^{-4} or approximately twice the value obtained experimentally. This agreement is excellent.

It should be noted parenthetically that although m will be independent of the composition of the gas phase, the values for the concentrations of C and FeO will change very markedly as indicated in Table 2.

TABLE 2.—*Calculated Concentrations of C and FeO in Iron Under Various Mixtures of CO and CO_2 at 1550° C.*

CO_2, Per Cent.	C in Metal, Per Cent.	FeO in Metal, Per Cent.	m = (C)(FeO)
6.0	0.0036	0.27	0.00098
0.6	0.041	0.024	0.00098
0.06	0.41	0.0024	0.00098
0.006	4.1	0.00024	0.00098
(0.000)	(5.6)		

As the table indicates, it is impossible for pure CO to exist in the presence of iron; as the amount of CO_2 in the gas decreases and approaches zero, the FeO concentration likewise approaches zero and the C concentration approaches the saturation value of 5.6 per cent.

That the gas in contact with the liquid iron in these experiments was not pure CO can be shown by calculation using the equilibrium constants given above. It is possible to make independent calculations using both the FeO and the C analyses of the melts. Results are as presented in Table 3.

TABLE 3.—*Calculated CO_2 in Gas Phase from Metal Analyses*

Run No.	CO_2 in Gas, Per Cent.	
	From C Analysis	From FeO Analysis
1	1.0	0.44
2	1.0	0.34
3	1.2	0.44
5	1.2	0.53
6	1.0	0.46
7	1.0	0.56

The slight difference between the values thus independently obtained is well within the limits of error in analysis and indicates the essential correctness of the assumptions.

The figures given and the statements made in this discussion are in no way intended as adverse criticism, but should serve to emphasize the complexity of the problem and the great experimental difficulties which must attend a rigorous treatment of a system of this nature.

The calculations are based on data obtained for the most part at relatively low temperatures and no claim is made for the absolute accuracy of the results. The writer believes, however, that the general conclusions reached are entirely correct.

A. B. KINZEL.—Mr. Gaines has done a great deal of serious work on the subject and I appreciate his comments. It must be remembered that in his calculation the equilibrium values for the reactions are extrapolated, so that probably part of the remarkable check is due to the method of extrapolation.

In work of this kind not only must experiments be carefully planned, but they must be carried out with very great care and the technique of the operator must be good. Mr. Egan actually carried out practically all of the runs personally, and I attribute a great deal of the uniformity of the results to the excellent technique at his command.

Regarding the last three runs and the fact that the values go up very slowly, we feel that in this measurement if we have established the order of the phenomena, we have done a service. There is room for much more work. Further work and greater refinement will mean a completely different type of experimental set-up with the refinements that go with it. It is a more tedious type of work, and we believed that it was not justified, because there were so many other things we wanted to know about the open hearth, where the time and energy expended would be more fruitful. We make no claim for the accuracy of 5×10^{-4}. What we do claim is that it is in the region of 10^{-4}; about 5 ± 1, or 2.

R. S. DEAN, Chicago, Ill. (written discussion).—This paper certainly represents a step in the right direction: namely, the accurate laboratory determination of constants which have heretofore been assumed or approximated from actual furnace, data. However, the difference in magnitude between the authors' values and those approximated by Herty from furnace data is so large that we are justified in looking perhaps supercritically into their work. It is evident from Table 1 that the concentration of both C and FeO are constant, in fact more constant than their product m. This constancy of both C and FeO indicates, of course, that some other limiting condition has been put on our system other than that imposed by the reaction

$$FeO + C \rightleftarrows Fe + C$$

This additional restriction is probably a fixed $\frac{CO}{CO_2}$ ratio. If this ratio is an equilibrium ratio, it is, of course, clear that the value of m will be correct even though FeO and C are fixed. We do not, however, get the self-checking feature of a constant product of varying factors. If, however, the $\frac{CO}{CO_2}$ ratio is not in equilibrium at the temperature of the molten metal but is determined by some other factor as diffusion of CO_2 from the colder portions of the furnace where the reaction $CO \rightarrow C + CO_2$ goes on, then the values of m determined may be much too low.

The check value obtained by passing a stream of gas through the furnace is an argument against such an assumption but before accepting so low an equilibrium constant, it should be checked under conditions where both C and FeO may be widely varied.

A. B. KINZEL (written discussion).—Mr. Dean's discussion is appreciated and is very much to the point. We too have noted the restrictions as to the iron oxide and carbon which seems to be applied by the fixed CO: CO_2 ratio. Within the limits of experimental accuracy, it seems to us that we do get a constant product and that we should expect to get such a constant product due to the relatively small influence of minor variations in the ratio. We also believe that the check value obtained by passing a stream of gas through the furnace is a much stronger argument against Mr. Dean's assumptions than he seems to believe. I should like to point out that while the final conditions showed carbon and FeO in a narrow range, the initial conditions were such that the carbon and FeO were widely varied as Mr. Dean suggests. The difference between the values obtained in this work and those approximated from fur-

nace data is in our opinion, due to the lack of equilibrium in the open hearth. Thus, the open-hearth values as approximated by Herty are probably correct for conditions as they exist but these are not equilibrium values.

We agree with Mr. Dean that there is still much to be learned regarding the whole problem, but we do believe that the order of magnitude of the equilibrium constant is fairly well established. We hope that in the work Mr. Dean is about to take up he may find the occasion to check our work so as to more firmly establish the true value of the constant in question.

H. W. GILLETT, Columbus, O.—Is it not possible to analyze directly for CO_2 and settle the question?

A. B. KINZEL.—That is an excellent suggestion but it is a little more difficult to do with the particular type of apparatus that we had at our disposal than it would seem at first glance. Because in all probability the $CO:CO_2$ ratio throughout the furnace is not constant we believed that the figure would have little value.

H. STYRI, Philadelphia, Pa.—In addition to what has already been said in the two written discussions, there may be a possibility that the heat of combination between the carbon and the iron influences the difference between the calculated carbon and the carbon actually found. That is very small, of course, and we may assume that under pure CO the carbon monoxide should dissolve approximately in atomic relation, 1C to 1O.

In a paper I published six years ago there is a sentence that concerns this subject.[7] I said: "For determination of equilibrium concentrations of silicon, manganese, and carbon in the steel, and FeO, Mn, and SiO_2 in the slag, by laboratory experiments, it should be more desirable to work under a gas of CO at 1 atm. than under a vacuum." At that time a calculation was made of the equilibrium constant, m as you call it, assuming carbon and oxygen going into the steel in equivalent ratio. Of course, the correct expression for m is actually the concentration of carbon times concentration of oxygen over carbon monoxide pressure. In my paper this concentration was given in parts, not in percentages, and in parts it was calculated at 0.000000011. Changing that into percentage for both O and C we strike out the four first noughts, and get 0.00011. Applying further the ratio FeO to O, which is 4.5, we find that it is equal to 5×10^{-4}.

That is, of course, too good to be true, and actually at that time the oxygen content was estimated as 0.0025 parts, which was 0.25 per cent. where Dr. Herty has found 0.3 per cent. That would raise the constant about ⅕, and if you figure it out for 1550°, the constant is still a little higher.

Of course, Dr. Kinzel has not seen this, perhaps because the paper is rather old and published in England. It was presented in preliminary form to the American Institute of Mining Engineers in 1919 but was rejected because it was not correct. In 1922 it was presented to the American Iron and Steel Institute calculated in more detail, and these figures were given, and it was rejected "because it was not correct."

A. B. KINZEL.—I want to compliment Dr. Styri. Some of you may know that at Columbia University they are starting work on the physical chemistry of steelmaking under the direction of Dr. Jette. I have discussed this matter in detail with him and he has pointed out one interesting phase which none of us have particularly considered before regarding this work, but which Dr. Styri has just touched upon; that is, that we are ending with low carbons, probably on account of the way we carry out the experiments. That is all right as far as the equilibrium value is concerned, taking conditions as we have them. However, in an open-hearth furnace, the heat is finished with high

[7] H. Styri: Theory and Practice of Steel Refining. *Jnl.* Iron & Steel Inst. (1923) **108**, 216.

carbon. Due to the Fe_3C reaction, it is possible that the equilibrium value would be different with the high carbon. It will be different, although it is of the same order of magnitude as that found in the paper.

C. H. HERTY, JR., Pittsburg Pa.—What about the solubility of CO as shown by your experiments, Dr. Kinzel?

A. B. KINZEL.—In iron free from the usual metallics and non-metallics that we have in the open hearth, it would seem to be quite evident from the results that are obtained that the solubility of CO must be very low. I cannot say anything further than that.

Regarding the failure to mention calculations made by Mr. Le Chatelier, we were aware of them although we did not study them in great detail because the figures on which they were originally based have been revised since that time. I am not sure about that in regard to Dr. Styri's calculation. He may have the figures which were revised just about the time his paper came out.

C. H. HERTY, JR.—The important application of Dr. Kinzel's work is that it apparently shows that the solubility of CO is very low in steel. I do not believe that the presence of 0.10 per cent. carbon, 0.08 manganese, 0.03 sulfur and 0.01 phosphorus is going to change that very markedly.

This upsets all our conceptions of what happens to steel in the mold, particularly in rimmed steels. Until recently I had considered that the rimming action in rimmed steels was due to one or both of two possibilities: (1) CO eliminated on solidification owing to drop in the solubility of CO in the metal when it passes from the liquid to the solid state, and (2) CO developed in the reaction between carbon and FeO in the metal, particularly at the solidifying surface. Now Kinzel's work shows fairly clearly that there is no ground for assuming a drop in the solubility of CO on solidification in so far as rimmed steel is concerned. Therefore the explanation for rimming of steel in a mold, which of course applies equally well to a small test mold, is this: A solid surface is required to bring about the carbon-iron oxide reaction. In other words, the open-hearth bath is enormously higher in oxygen for a given carbon content than is required for equilibrium, as indicated by Kinzel's measurements, but if a rod is put into the furnace to stir the heat there is a violent boil as the reaction toward equilibrium is accelerated. When the steel is poured into a mold and solidification begins there is a heavy reaction at the solidifying surface. This accounts for the importance in making rimmed steel heats of having a certain type of boil in the furnace and then adding enough manganese with a little aluminum to reduce the action somewhat.

If the FeO content of the metal in the furnace is controlled by regulating the composition and viscosity of the slag and the magnanese addition, the making of rimmed steel in the mold can be better controlled. For example, suitable gas evolution to give a good rimmed steel may result if the metal contains 0.15 per cent. FeO and 0.10 per cent. carbon at the time it is poured into the mold. It is obvious that if one heat contains 0.10 per cent. FeO, another 0.30 per cent., and another 0.25 per cent., and 800 lb. of manganese is added to all three of these heats, different rimming actions will result. The CO solubility is too low to affect the amount of gas given off, so that the amount of FeO is the determining factor. This is the answer, I think, to the problem of making rimmed steel. The problem should be better understood when more is known about the effect of slag viscosity and slag composition on the degree of saturation of FeO in the metal.

G. B. WATERHOUSE, Cambridge, Mass.—How soon will someone tell us how to take a test from a bath of metal, how to cool it, how to drill it, and then make a quick determination of the FeO in the metal?

C. H. HERTY, JR.—We have cut the time considerably in the last six months, but have not yet cut it to the time that you can get out control analyses. However, I believe it is unnecessary to go into the metal to take the sample. By taking the slag and using inclined planes for the viscosity, and on the basis of the FeO content, I think it will be possible to tell very accurately the percentage of iron present in the bath. We can do that in 15 minutes.

S. EPSTEIN, Chicago, Ill.—How close can you come to knowing how much FeO there is in the metal from the amount of FeO you find in the slag? If in an electric furnace you have a carbide slag, and you keep it on for a considerable length of time, are you sure that you know the FeO content of the metal?

C. H. HERTY, JR.—Carbide and rimmed steel are two very different things. You can certainly say this: if there is a certain amount of FeO in the metal, and aluminum, or silicon, or manganese is added, you deoxidize. If there is a very low FeO in the bath you will not deoxidize with the same amounts of silicon, aluminum, or manganese. In other words, the lower the FeO in the metal, the more aluminum or silicon must be added to do any deoxidizing; and that, I think, is the reason for the low FeO content of electric-furnace steels, and the fact that deoxidizers must be added.

S. EPSTEIN.—There may not be as much iron oxide in electric-furnace steel as there is in rimming steel, but if a sample is taken from the basic electric furnace after a carbidic slag has formed but before the bath has been deoxidized, it will be found on microscopic examination that a considerable number of iron oxide particles are present in the metal.

C. H. HERTY, JR.—Are you sure it is iron oxide? I do not believe it is, not in carbide slag, because the solid solubility of iron oxide is sufficiently high that up to an appreciable amount it cannot be seen at all. Manganese oxide in very fine particles looks much like iron oxide.

S. EPSTEIN.—Why should you find manganese oxide?

C. H. HERTY, JR.—There is manganese in the metal and as long as there is manganese, there must be maganese oxide. Manganese oxide is less soluble in liquid steel than iron oxide. So if there is 0.10 per cent. FeO in the liquid steel and 0.03 per cent. in the solid steel, I think that probably you could not see the iron oxide in the solid test, but that you could see the MnO on account of its low solubility in solid steel.

A. HAYES, Middletown, O.—What is the source of the data that Mr. Gaines used in calculating the equilibrium constant for FeO, CO and CO_2?

C. H. HERTY, JR.—Mr. Gaines used the data of Garran,[8] and of Lewis and Randall.[9]

A. HAYES.—Was that equilibrium studied with the pure phase FeO?

C. H. HERTY, JR.—Yes.

A. Hayes.—The work which I have done in this field in connection with the physical constants of iron carbide, and the statements I find in the literature are to the effect that it is impossible to maintain the pure phase FeO in contact with CO and CO_2, that it is impossible to keep it from going over to a mixture of FeO and higher oxides, in which case the equilibrium constant would correspond to a higher CO_2 constant for that particular reaction. This should be the case, and if it were so instead of 1 by 10^{-4} it might come down much nearer to the value that Dr. Kinzel has shown, and agree much more nearly with the value Dr. Styri also calculated from an early diagram.

Another question, what would the diffusion coefficient of FeO between electric-furnace slag and the bath and the open-hearth slag and the bath?

C. H. HERTY, JR.—We have not done any work on electric-furnace slag, Dr. Hayes.

G. B. WATERHOUSE.—I assume this in both cases is basic?

A. HAYES.—The same thing that Dr. Epstein discussed.

C. H. HERTY, JR.—The distribution coefficient was determined under three types of slags: pure iron oxide, so that we knew the true solubility relationship; lime iron oxide, that is, only lime and iron oxide, so we knew the mol fraction of FeO; and third, the acid slags of FeO and silica. With the acid slags the solubility was much lower than on the basic slags. What we want to know about basic electric-furnace slags is not the distribution ratio but the mol fraction of FeO in the slag.

A. HAYES.—If you knew the FeO content, that is the mol fraction of the FeO in the slag of which you are speaking, it would then be necessary to establish the fact that FeO as a molal constituent in the slag behaves as an ideal solute, and I wonder if that has been established.

C. H. HERTY, JR.—We took a lime-FeO slag. We went from zero to 40 per cent. lime, and from 100 to 60 per cent. FeO, and in all that series of experiments the distribution ratio was the same as it had been under pure oxide slag, indicating that for that type of slag it was the same.

I think that the activity and the mol fraction are fairly close together over the range, but that in the case of carbide slags and open-hearth slags, we do not know the true mol fraction of FeO in the slag. We assume that in 20 per cent. iron oxide slag in the open hearth we have calcium silicate, and everything else is dissolved in it. Now the chance of having that is small, so that the mol fraction of FeO in open-hearth slag is probably a little higher than calculated.

A. HAYES.—There might be a higher iron oxide content in the electric-furnace heat corresponding to a given iron oxide content in the electric-furnace slag than there would be for corresponding temperature in the open-hearth slag. Or we can calculate the difference in distribution coefficient for a given mol fraction, because in the ordinary solutions with which we work in water—that is the one solvent that we do know most about—we find that wide discrepancies exist between the predicted activity of a constituent solution as calculated from its mol fraction and the actual measured activity, and we recognize the fact that deviation is due to a failure of the solute to follow the laws of what we call ideal solution. I should think it would be necessary to demonstrate the fact that its distribution coefficient is always the same with the same mol fraction of FeO in the slag for different slags.

C. H. HERTY, JR.—It would be even more important to determine the diffusion coefficient over the range of 60 per cent. FeO to zero.

A. HAYES.—With the constituent, and FeO and CO.

C. H. HERTY, JR.—We are working on different types of slags now. We started with pure iron oxide, and now we are going to iron silicates and iron oxide. We have gotten the same distribution coefficient over a range of 100 to 50 per cent. FeO at the same temperature.

H. STYRI.—There is one thing more in the determination of oxygen in steel that perhaps ought to be pointed out. The total quantity of oxygen is always determined

[8] R.R. Garran: *Op. cit.*

[9] G. N. Lewis and M. Randall: *Op. cit.*

but the amounts combined with silicon and manganese and iron are not distinguished. If the percentages of oxygen combined with silicon and manganese present are not given, the amount of oxygen free to react with carbon is not known.

C. H. HERTY, JR.—With the microscope it is easy to determine how much is present as iron silicate. I cannot tell as closely how much is present in MnO and the percentage of iron silicate is so small that it does not amount to much in the total. The MnO unquestionably amounts to more than the iron silicate.

MEMBER.—I was much interested in the discussion by Dr. Herty of the solution or solubility of carbon monoxide in the liquid steel at the point of solidification, and his explanation of the giving off of the gas as a result of the reaction of the iron oxide with the carbon.

Inasmuch as it is generally considered that the reaction of iron oxide and carbon takes place more rapidly at the higher temperature, I would like to ask him if he has any explanation as to why this violent evolution takes place at the solidification point when the temperature is very low.

C. H. HERTY, JR.—That was discussed at the February, 1929, meeting, and we have no explanation. There are two or three things to be considered, one of which is simply the effect of reaction taking place on a cold surface more rapidly than it does in a solution. The surface combustion feature depends on a brick wall to make that combustion more rapid. If you put a rod into the bath and get the boil on the rod, in the furnace and in the ingot mold the action is the same makes it possible that something like that is happening. If you take a little something to start the reaction, it goes right ahead. The same way with the boil on the bottom.

G. B. WATERHOUSE.—Regarding the difficulty of getting an open-hearth bath below a fairly low carbon, referred to at the beginning of the paper: Have you any really good ideas on how to knock that carbon down below 0.07, 0.06, or 0.05 per cent. in a reasonable time?

A. B. KINZEL.—To answer categorically, no, but it would appear that some method of highly oxidizing so as to get the carbon down, then deoxidizing with some element other than carbon is one possibility. Increasing the rate of reaction by some phenomenon similar to that of sticking the rod in the furnace to accelerate this reaction and make it come down to equilibrium is another possibility. All those who have worked around an open-hearth furnace know how difficult it is actually to do any real work with the bath in that way. Possibly some such method will be developed. I have no practical suggestion at this time.

A. HAYES.—In regard to the question about the violent evolution at the solidification point, if we assume that iron oxide and carbon are both less soluble in the solid than they are in the liquid phase, then as solidification proceeds the concentration of these different constituents will be increased and the liquid that remains moves the concentration of the two reactants in the reaction under discussion to values where it is possible for reaction to proceed, and I rather suspect that that is a part of the explanation of the rapid evolution of gases during solidification.

S. EPSTEIN.—Has a possible effect of oxygen present in the electrolytic iron been considered? You speak of electrolytic iron as though it were pure iron with no other element present, but I have always found that it contains an appreciable amount of iron oxide.

A. B. KINZEL.—That is an important point which we have considered. Not only is oxygen present in the electrolytic iron, but quite often carbon, and we have attempted to eliminate these by first vacuum-fusing and holding for an appreciable

length of time before starting the experiment. As to the material not extracted in the Torricellian vacuum, we believe that the equilibrium conditions in the experiment proper would take care of that.

A. HAYES (written discussion).—In a discussion of the causes of evolution of gases from live steel with Dr. Herty after the meeting at which the paper by Messrs. Kinzel and Egan was presented, he pointed out the fact that gases are evolved about an iron rod when it is placed in liquid metal and held there long enough so that there is no solidified metal remaining on the rod. In fact, he says that gases are evolved even after portions of the bar have been melted away.

If this is true, I wish to suggest that in the reaction

$$FeO + C \rightarrow Fe + CO$$

pressures of CO must occur of sufficiently high values to start the formation of bubbles of CO, whose radii are smaller within the volume of the liquid.

As can be readily shown, the pressure necessary to overcome the surface tension of the liquid is inversely proportional to the radius of the bubble and can be expressed through the equation

$$p = \frac{2\gamma}{r}$$

where γ is the surface tension.

It is due to this fact that sharp-pointed objects placed in boiling liquid causes it to boil smoothly. Also, these objects which are placed within the boiling liquid present points of contact with the liquid which have radii of appreciable values, off of which bubbles may be formed.

The effect of the foreign body such as the rod placed in the live steel, together with the fact that in practically all open-hearth heats the product of FeO × C is many times larger than the equilibrium constant which Dr. Kinzel has obtained, and the further fact that during the solidification process both FeO and C are concentrated in the liquid phase, constitute perhaps a satisfactory explanation of the evolution of gases from live steel during the pouring and solidifying processes.

Pure Iron and Allotropic Transformations

By T. D. Yensen,* East Pittsburgh, Pa.

(New York Meeting, February, 1929)

If the question should be asked at this time: "Does pure iron have allotropic transformations?" the reply would necessarily be, "We do not know." And it is doubtful whether anybody, anywhere, is in a

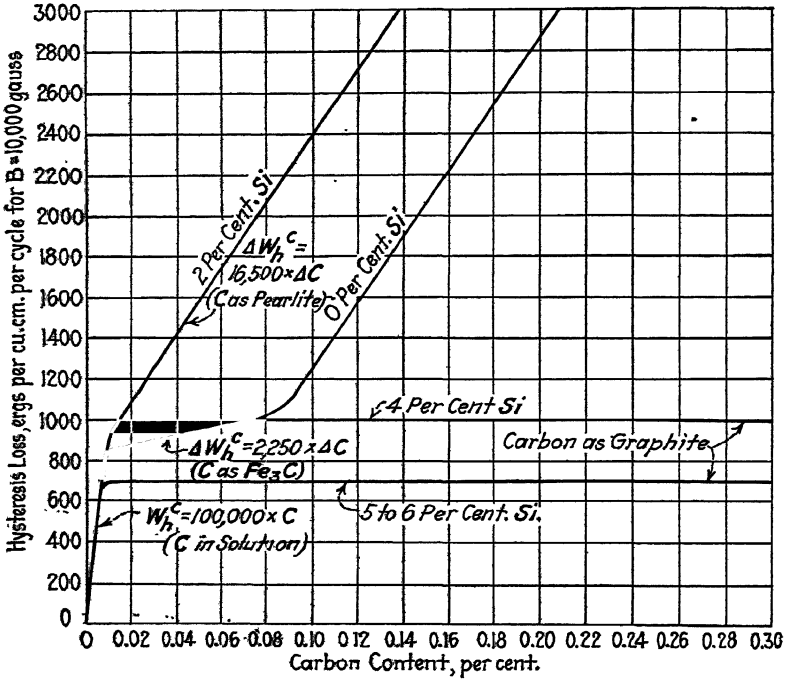


Fig. 1.—Effect of carbon on hysteresis loss of iron-silicon alloys. (All other impurities and effect of grain size eliminated.)

position to make any other reply at this time, for the simple reason that pure iron has not yet been made and tested. The nearest approach to it contains either an appreciable amount of carbon or else an appreciable amount of oxygen (a few hundredths of a per cent.). But why be con-

* Research Laboratory, Westinghouse Electric & Manufacturing Co.

cerned with such small amounts of impurities? Aside from the strictly scientific importance of the properties of pure iron it is of practical value to know that very small amounts of these impurities may have a tremendous effect on its physical characteristics. Fig. 1 will serve as an illustration, showing the effect of carbon on the magnetic properties of iron. Iron with 0.008 per cent. C is commonly regarded as pure iron. But we see from Fig. 1 that for every 0.001 per cent. C removed from the above value the hysteresis loss of this pure iron is reduced by about 10 per cent. This large effect is due to the fact that carbon in amounts less than 0.008 per cent. is in solid solution in the iron, *i. e.*, it is a part of the iron lattice. Indications are that small amounts of oxygen or nitrogen are equally effective.

With these facts and indications in mind it seems logical to suppose that other data pertaining to supposedly pure iron may not apply to actually pure iron, and the purpose of this paper is to erect a question mark in our minds in regard to the firmly rooted idea that pure iron necessarily has allotropic transformations. If the author can produce skeptics as to this orthodox belief he shall have accomplished his purpose for the present. Investigations will then be launched that will in a short time result in proving or disproving the point in question.

Evolution of the Iron-carbon Diagram

Structural changes taking place in iron at various temperatures below the melting point have been known since 1864, the beginning of the science of metallography. Some of these changes, the A_1 and A_2 transformations, were found to be invariant with respect to the carbon content while the others, the A_3 and A_4 transformations, appeared to be a function of the carbon content. (Fig. 2.)

It was soon discovered that the A_2 transformation occurring at about 780° C. was associated with the appearance and disappearance of ferromagnetism, and it was at first supposed that the transformation involved a change in the crystal structure. The application of X-ray analysis, however, revealed the fact that this is not the case, alpha and beta iron both having body-centered cubic structures, and if we define allotropic changes so as to involve changes in the lattice structure then the A_2 transformation is not an allotropic change. The A_2 transformation may be associated with a change in the structure of the iron atom not detectable with X-rays, or it may be the point at which the thermal agitation of the atoms prevents their orientation in a magnetic field. The elimination of the A_2 transformation point leaves the A_1, A_3 and A_4 as the true allotropic transformations in iron.

Consider next the A_1 point, which was found to be due to the precipitation of cementite (Fe_3C) from the solid solution of austenite (gamma iron)

with about 0.85 per cent. C at about 700° C. The resulting structure was called pearlite and consists of an intimate mixture of ferrite (alpha iron) and cementite. As austenite (gamma iron) has a face-centered cubic structure, this transformation is a true allotropic change. However, as the carbon content as time went on was decreased to lower and lower values, the A_1 transformation was found to disappear for a carbon content of less than 0.05 per cent. The author's work on the magnetic

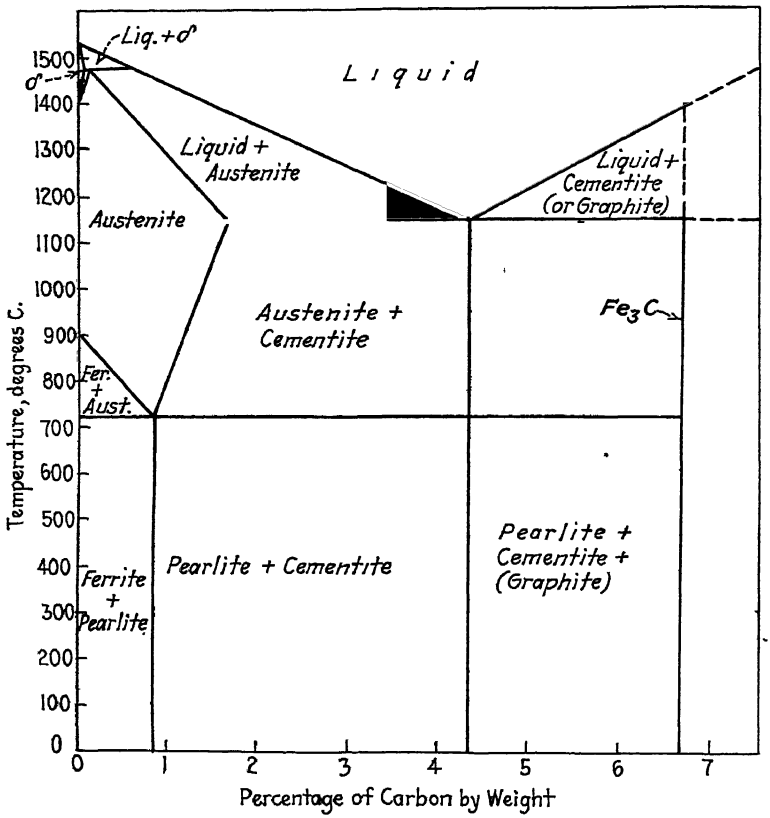


FIG. 2.—CLASSICAL EQUILIBRIUM DIAGRAM FOR IRON-CEMENTITE SYSTEM

properties of Fe-Si-C alloys[3]* gave the first indication that carbon is not insoluble in iron at ordinary temperatures, but remains in solution up to about 0.008 per cent. (Fig. 1). That the solubility should be 0.05 to 0.08 per cent. as held by Sauveur and Krivobok[4] and by Hatfield[5] does not seem probable and must rest on a misinterpretation. For very low carbon iron we are consequently left with only the two allotropic transformations, the A_3 and A_4. These are the ones we shall be largely con-

* Superior numbers refer to references at end of paper.

cerned with in this paper and the attempt will be made to show that for pure Fe even these transformations may not exist.

According to the orthodox view the solubility of carbon in alpha iron at 905° C. and in delta iron at 1400° C. is zero, and even pure iron is supposed to pass through allotropic transformations on cooling at these temperatures (from delta to gamma at 1400° C. and from gamma to alpha at 905° C.). There is apparently good reason for this assumption, because these transformations have always been found for iron, no matter how low the carbon content. However, there are other elements present in iron, whose effect on the transformations we know very little about as yet. One of these elements is oxygen, and the lower we make the carbon content the higher we probably make the oxygen content, unless precautions are taken greater than any that have been taken in the past. In the author's early experiments with electrolytic iron and vacuum melting he invariably found that a certain amount of the deoxidizer (C, Si, B, Al, etc.) was lost during the melting, corresponding to about 0.4 per cent. oxygen.[6] This has been confirmed by all of his later work[3] and also by that of the author's associate N. A. Ziegler, after taking the utmost care to remove all surface oxidation from the iron and using the most improved method of melting, the high-frequency bell jar type of vacuum furnace.[7] That the effect of this oxygen on the physical properties of iron is very large is shown by the following experiment:

Mr. Ziegler prepared a number of samples in the bell jar furnace using electrolytic iron and carbon in various small amounts up to 0.5 per cent. No carbon above that usually found in electrolytic iron (0.005 per cent.) was found in any of the samples except those to which more than 0.3 per cent. was added. Test rings were machined, annealed and tested magnetically. The maximum permeability increased with additions of carbon from about 25,000 for 0 per cent. C added and reached a maximum of 61,000 for 0.06 per cent. added, from which point the values again dropped very rapidly. The value 61,000 is much higher than has ever before been obtained for unalloyed iron and can be explained only on the basis that for this sample, by a coincidence, the correct amount of carbon was used so as to decrease materially the oxygen content without leaving more than about 0.005 per cent. carbon in the iron.

The disadvantage of using carbon rather than silicon is that if too much carbon is added (0.01 per cent. excess would be sufficient to ruin the magnetic properties) it can not be removed without excessive oxidation. Here, then, we have a bit of indirect evidence to the effect that the purest iron obtainable contains a relatively large amount of oxygen, and that this oxygen, which is ordinarily overlooked, has a very large effect on the physical properties of the iron. This being the case is it not reasonable to suppose that the oxygen also has correspondingly large

effect on other properties and actually may be responsible for the A_3-A_4 transformations usually found in very low carbon iron?

In order to explain the large effect of oxygen it must be assumed that it is in solid solution in the iron, and we must therefore inquire into the evidence available as to this point.

Recent investigations by Tritton and Hanson[8] at the National Physical Laboratory and by Jordan and Eckman[9] at the Bureau of Standards indicate that the solubility of oxygen in iron at 20° C. is 0.02 to

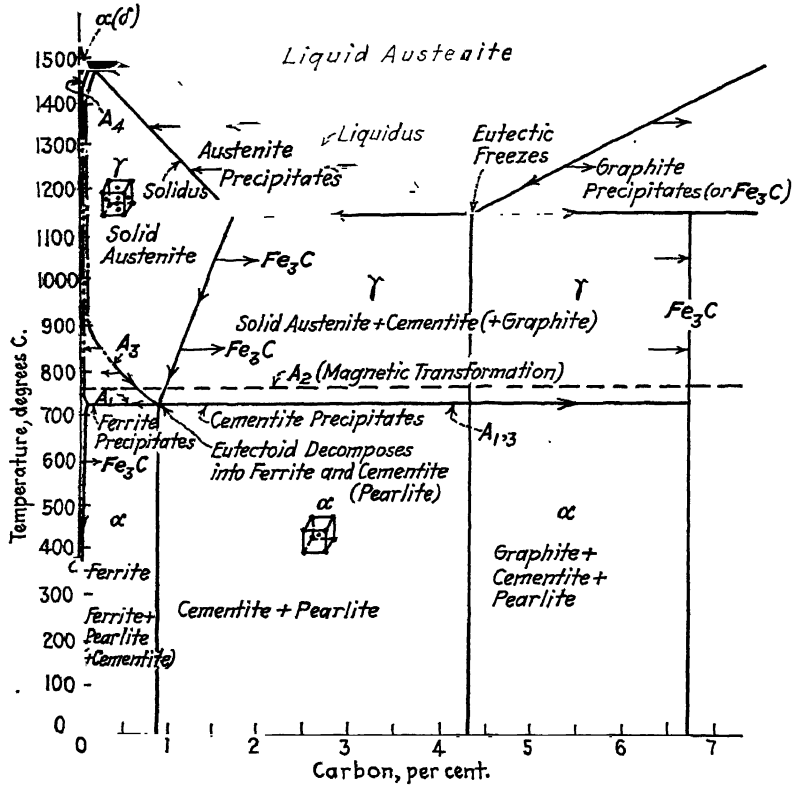


FIG. 3.—CONSTITUTIONAL DIAGRAM FOR FE-C.

0.05 per cent. and at 1530° C. about 0.2 per cent. There may be some question as to the exact figures for the solubility, as the results will depend on the method of analysis and also on possible changes in oxygen content between the metallographic test and the analysis. Oxygen analysis constitutes one of the most difficult problems to be dealt with in connection with iron research work. It is sufficient, however, for the present to know that we have good evidence that oxygen is soluble in iron to some extent, and that the measurements of the critical points made with so-called "pure" iron (meaning thereby iron with traces of

C, S, P, Mn, etc.) in reality are measurements made with more or less saturated solutions of Fe and oxygen.

Tritton and Hanson,[8] for example, investigated the effect of oxygen on the transformation points and found no change in the A_3 points. But the oxygen range in their samples was 0.09 to 0.21 per cent. O_2, the lower limit of which probably is close to the maximum solubility at 900° C., so that they missed the most important range, namely that in which the oxygen is in solution.

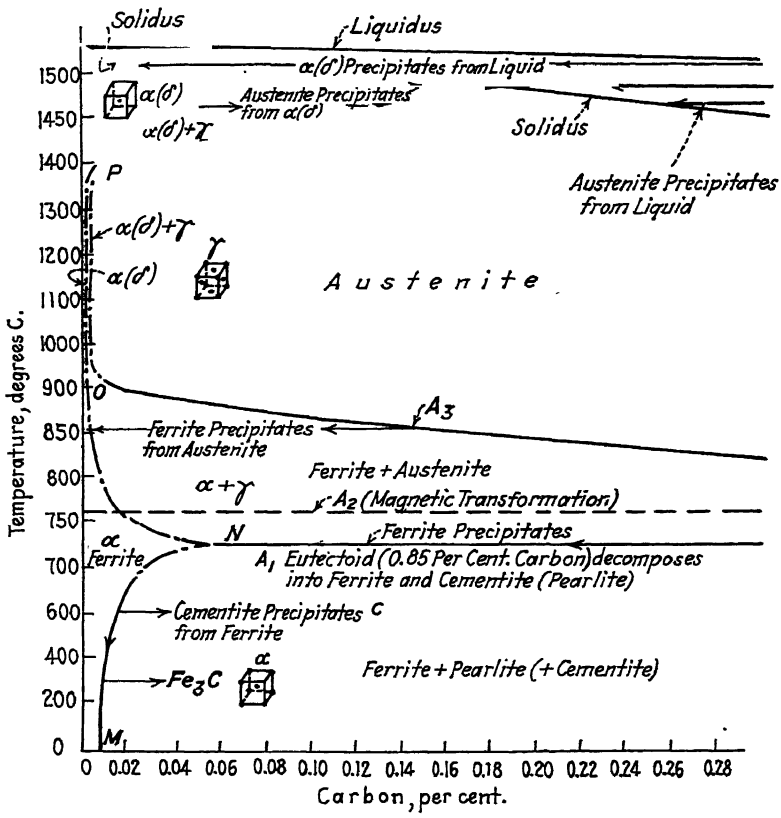


FIG. 4.—CONSTITUTIONAL DIAGRAM FOR FE-C.

It is consequently safe to say that we have so far no *direct* evidence, one way or the other, that pure iron (Fe) has allotropic transformations. The indirect evidence, however, obtained from the metallographic investigation of iron-silicon-carbon alloys has led the author to construct the equilibrium diagram as shown in Figs. 3 and 4, showing the possibility of pure iron having no allotropic transformations. But before proceeding to this indirect evidence it seems desirable to consider briefly the question of solid solubility, what this means and the consequences of our definitions and interpretations.

Solid Solubility

Solubility is generally defined as the property of one element mixing with another in continuous proportion in such a way as to form a homogeneous aggregate. When we consider solids made up of atoms arranged in definite crystal lattices we must, however, distinguish between two kinds of solid solutions: (1) those in which the solute is a substitution element and (2) those in which the solute is an interstitial element.

A *substitution element* is one whose atoms enter the crystal lattice of the solvent and occupy some of the places in the lattice previously occupied by the solvent atoms. Ni and Fe are two such elements, soluble in each other in all proportions at all temperatures. Let us consider this system as a typical example.

Assume for the sake of this discussion that the Fe-lattice consists of body-centered cubes. As we start to add Ni-atoms to 100 per cent. Fe, they will distribute themselves (if given time and favorable conditions) uniformly among the Fe-atoms; *i. e.*, as we pass along the lattice structure we shall meet at regular intervals a Ni-atom instead of an Fe-atom. There seems to be no strong tendency for the Ni-atoms to associate themselves with a definite number of Fe-atoms to be segregated in the form of compounds. If compounds were formed we should expect the intermediate alloys to consist of mixtures of two compounds with a eutectic and we have definite indications that this is not the case. We must, therefore, assume that in this case the forces of combination are not sufficiently strong to overcome the forces of diffusion.

On the other hand, as the Ni content approaches 30 per cent. there is a chance for homogeneity to be established, provided the lattice be changed from body-centered to face-centered. Without going into a further detailed discussion it may be pointed out that in the Fe-Ni system we have the possibility of homogeneous arrangements of the atoms in the space lattices for the following compositions: Fe (body-centered cube), Fe_3Ni (26 per cent. Ni, face-centered cube), FeNi (51 per cent. Ni, face-centered cube), $FeNi_3$ (76 per cent. Ni, face-centered cube) and Ni (face-centered cube).* While the intermetallic compositions are written Fe_3Ni, $FeNi_3$, FeNi, they may be regarded either as very weak compounds or merely as certain stages in the continuous solid solutions from pure Fe to pure Ni.

An intermetallic compound may consequently be regarded as a solid solution in which the forces of combination are stronger than those of diffusion. The stronger the former, the greater is the concentration range from which the compound is precipitated.

* Is it merely a concidence that the above ranges roughly correspond to the ranges for the nonmagnetic alloys (28 per cent. Ni), and the two highly magnetic alloys hipernik (50 per cent. Ni) and permalloy (78½ per cent. Ni)?

When we come to the Fe-Si system, the situation is evidently different from the one just considered. Silicon is also a substitution element in its relation to iron, but in this case the forces tending to form the combination FeSi (33 per cent. Si) are very strong, resulting in a eutectic containing about 20 per cent. Si, with a melting point 200° and 300° lower than those of FeSi and Fe, respectively.

It should be noted that Fe and Ni are similar elements while Fe and Si have quite different characteristics.

An *interstitial element* is one whose atoms enter the solvent lattice and occupy the open spaces between the solvent atoms. Carbon is perhaps the best known element belonging to this class in its relation to iron[10,11]. However, the solubility of carbon in iron is very low, a maximum of perhaps 0.1 per cent. in the body-centered cube and 1.7 per cent. in the face-centered cube (Fig. 4). For higher concentrations the tendency to form a compound is greater than the tendency for diffusion with the result that Fe_3C containing 6.67 per cent. C is segregated or precipitated from the solid solution. The structure of this compound, according to Westgren and Phragmén[11] belongs to the orthorombic system.

Nitrogen is another interstitial element in its relation to iron. Its maximum solubility in alpha iron according to Fry[12] is about 0.5 per cent. at 580° C. and when the solubility is exceeded Fe_4N is precipitated which according to Hägg[13] has a face-centered cubic structure with the N-atom in the center of the cube. It was stated previously that the maximum solid solubility of oxygen in iron is of the order of 0.2 per cent.[8,9] and it is not improbable that its effect on the iron lattice is similar to that of nitrogen.

All these interstitial elements consequently enter the iron lattice in small amounts and in so doing produce a condition such as to cause a tendency for the lattice to change from the body-centered cube to the face-centered cube, in which the solubility for these interstitial elements is the greater.

Even with the maximum solubility, however, the concentration of the interstitial elements is very low. For example, in the case of the body-centered cube of iron at 1475° C. the solubility of carbon is about 0.08 per cent. which corresponds to one carbon atom to every 125 unit cubes, occupying a cube with 5 unit cubes along each edge. At a temperature of 1475° C. the thermal agitation of the atoms is very large and it is conceivable that the small carbon atoms travel from one cube to another with high velocity. At low concentrations, the carbon atoms may slip through the alpha lattice without permanently distorting it, but as the concentration is increased a point will be reached, depending on the temperature, for which the visits become too frequent for the alpha-lattice and the change to the gamma-lattice takes place. For still

higher concentrations even the gamma-lattice is insufficient and the compound Fe_3C is formed as already described.

The larger interstitial atoms like oxygen and nitrogen may not be able to pass through the lattice as readily as the carbon atom, and may be permanently attached to regularly spaced unit cubes. In so doing the "stranger" atom (adopting Rosenhain's terminology) may displace the central Fe-atom, which in turn displaces its neighbor and so on, until a number of these displaced atoms meet and form a face-centered cube. This action upsets the regularity of the whole lattice: the neighboring central Fe-atoms are displaced, and as more "stranger" atoms enter, more and more gamma-cubes are formed until the entire alpha lattice breaks down and the gamma lattice is formed with "stranger" atoms in the centers at regular intervals.

So far no mention has been made of the variations in solubility with temperature. Jeffries and Archer have treated this subject extensively in their book on "The Science of Metals," to which the author wishes to pay tribute. The general rules, based on Le Chatelier's principle, governing the effect of temperature on solubility, according to these authors, are: (1) If the excess constituent in equilibrium with the solution is a pure compound or element its solubility increases with rising temperature; (2) if, on the other hand, the excess constituent is itself a solution, the solubility decreases with rising temperature.

In view of the opinion expressed on page nine that there is no sharp line of demarcation between intermetallic compounds and solid solutions it seems to the present author that the above two principles can be combined into one, namely: The solubility of the elements of one constituent in another constituent will increase or decrease with rising temperature depending on the relative strength of the bonds between the elements of each constituent.

As distinct compounds or single elements have strong bonds, their solubility in a solvent will increase with rising temperature. Furthermore, the relative strength of the bonds between the elements of each constituent varies with the temperature, resulting in solubility lines that may first decrease and then increase or vice versa. Consider, for example, iron and carbon: as the temperature is increased from 725° C. the solubility of carbon in alpha iron decreases in agreement with Jeffries and Archer's second rule, the excess constituent being the solution of carbon in gamma iron. But, between 1400° and 1475° C., with rising temperature, the solubility of carbon in alpha (delta) iron increases, the excess constituent here being the same as above. In passing from 725° to 1400° C. a change evidently takes place in the relative characteristics of the two solid solutions. It need not be assumed that there has necessarily been a change in the lattice structure of either constituent. The evidence is all to the contrary. The explanation may well be found in a differ-

ence in the temperature coefficients of the strength of the bonds between the elements of the two constituents. The bonds of both may decrease but one more than the other.

Indirect Evidence as to Non-allotropy in Pure Iron, Obtained from Fe-Si-C Diagrams

It seems to be a well-established fact that with increasing silicon content the A_3 transformation point occurs at increasing temperatures and gradually disappears (Osmond,[14] Gontermann,[15] Charpy,[16] Charpy and Thenard,[17] Honda and Murakami[18]), while the A_4 point occurs at decreasing temperatures and gradually disappears (Ruer,[19] Sanfourche,[20] Wever and Giani,[21] Phragmén,[22] Hanson[23]). This evidence coupled with the fact established by Westgren and Phragmén[11] that the alpha and delta modifications are identical, naturally led to speculation as to the complete form of the Fe-Si equilibrium diagram, particularly in regard to the A_3 and A_4 lines. The evidence is sufficiently strong for justifying the conclusion that with silicon above a certain amount (1.5 to 2.5 per cent.) the A_3 and A_4 lines are joined and no gamma modification exists.*

The author has been engaged in the study of iron-silicon alloys since 1914, and has fully realized the necessity of a careful metallographic investigation of these alloys as a means towards an intelligent development of their magnetic properties. He has been fortunate in being associated with N. B. Pilling who, with the able assistance of G. P. Halliwell, undertook the metallographic work, as a result of which much valuable data have been obtained.[25] These have been extensively used in drawing the constitutional diagrams shown in this paper. Pilling and Halliwell, however, did not investigate the delta-gamma range, and the parts of the diagrams dealing with the solubility of carbon in alpha iron are based partly on data obtained from other sources[1,2,11,18–23] and partly on hypothesis.[26]

Fig. 5 is a superposition of several Fe-Si diagrams with carbon contents varying from 0.001 to 0.1 per cent. The uncertain parts are shown in dot and dash as in Figs. 3 and 4. Fig. 5 shows that the A_3 point increases rapidly with decrease in carbon below 0.05 per cent. for constant silicon, leading logically to the conclusion that the A_3-A_4 transformations depend on the carbon content in such a way that the lower the carbon the less silicon is require to eliminate them. This is undoubtedly one

* While Oberhoffer is given credit for being the first proponent of this theory (1924) it seems but fair to call attention to the fact that the possibility was suggested by Hanson in discussing the Westgren-Phragmén paper[24] in 1922, on the basis of which the present author suggested the absence of the transformations in his paper on Fe-Si-C alloys[3] in February, 1924.

of the reasons for the large variation in the reported values of silicon required to make A_3 disappear (1.5 to 2.5 per cent.).

If now a decrease in carbon from 0.1 to 0.01 per cent. decreases from 3 to 2 per cent. the silicon necessary to cause A_3 and A_4 to disappear, is it not logical to assume that a further decrease in carbon will further decrease the necessary silicon until in the limit with no carbon (or C less than 0.001 per cent.) no silicon is needed, provided oxygen and other interstitial impurities can be kept out? If this reasoning is correct, the

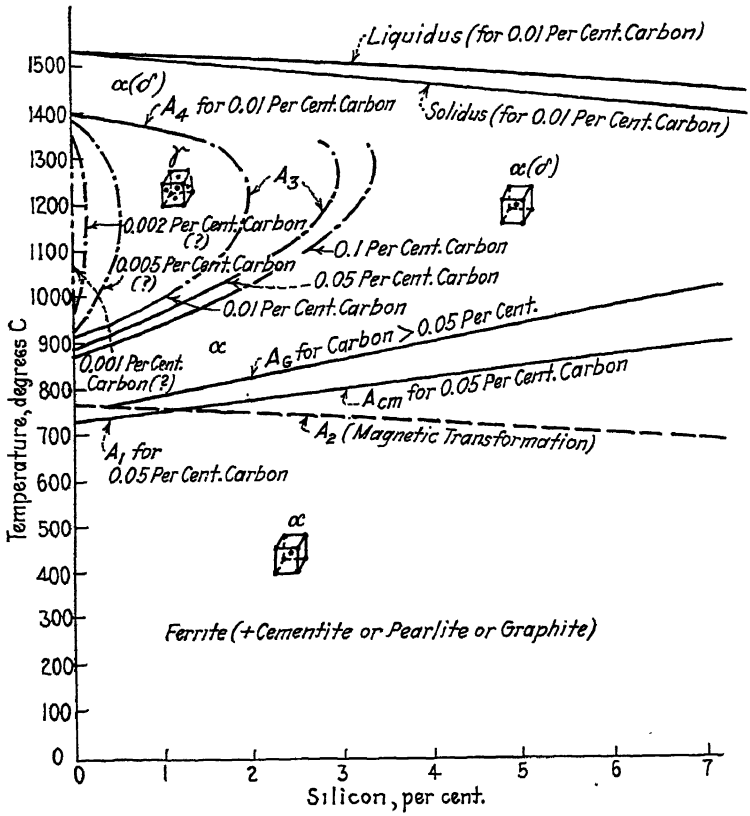


FIG. 5.—CONSTITUTIONAL DIAGRAM FOR FE-SI.

equilibrium lines for very low carbon for the Fe-C system should be as shown by *OP* in Fig. 4.

The question is naturally asked: Why should silicon produce this change in the properties of the Fe-structure? In the first place, as already stated, silicon enters the iron lattice as a substitution atom, *i. e.*, it takes the place of an iron atom. In so doing the characteristics of the lattice are changed to some extent, perhaps in such a way that the alpha modification can accommodate more carbon (in solution) before it has to change over to the gamma-form. In the second place, silicon is a strong deoxi-

dizer. This means that its affinity for oxygen is stronger than that of iron, resulting in a new constituent SiO_2 or $FeSiO_3$ appearing in the grain boundaries or, if conditions as to time and temperature are favorable, on the surface of the alloy. If oxygen is partly responsible for the A_3-A_4 transformations the removal of oxygen by silicon should consequently tend to eliminate them.

But why should such a relatively large amount of silicon (1.5 to 2.5 per cent.) be needed to remove a very small amount of oxygen (0.1 to 0.2 per cent.)? It is probable that even in the liquid state or at high temperatures in the solid state the rate of diffusion of both silicon and oxygen is insufficient to affect complete elimination of the oxygen atoms without excess silicon, and as the temperature drops, the rate of diffusion becomes gradually slower and the probability of a silicon atom and an oxygen atom meeting becomes correspondingly small, so that for the complete elimination of oxygen, the number of silicon atoms must be large.

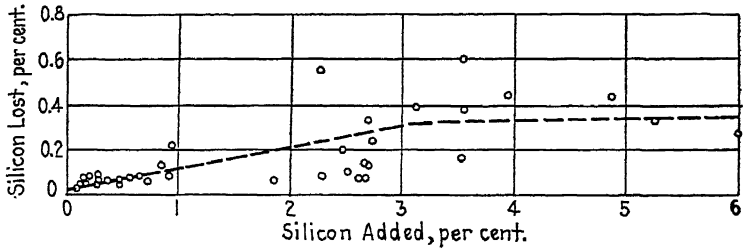


FIG. 6.—LOSS OF SILICON BY OXIDATION IN PREPARING IRON-SILICON ALLOYS IN ARSEM VACUUM FURNACE.[6]

Carbon is a much more effective deoxidizer than silicon or any of the other deoxidizers (Al, B, etc.) and its effectiveness is probably due very largely to its small size and consequent high rate of diffusion.

It was mentioned previously that electrolytic iron contains about 0.4 per cent. oxygen, requiring for its removal about 0.3 per cent. carbon. It was also mentioned that in a vacuum furnace carbon does not begin to combine appreciably with iron until all the oxygen has been eliminated.

Silicon, on the other hand, acts very differently. Fig. 6 has been plotted from the author's results[6] on iron-silicon alloys prepared in an Arsem vacuum furnace. While the points are scattered for high silicon additions there is an indication that the amount of silicon lost reaches a constant value of 0.3 to 0.4 per cent. (corresponding to 0.35 to 0.45 per cent. oxygen) for 2 to 3 per cent. silicon added. In other words, it requires 2 to 3 per cent. silicon to deoxidize the iron while the deoxidation can be accomplished with 0.3 per cent. carbon.

The correspondence between the 2 to 3 per cent. silicon required for deoxidation and the 1.5 to 2.5 per cent. silicon required for the elimination of the A_3-A_4 transformations should be noted.

While conclusive evidence of the absence of allotropy in pure iron in the form of heating and cooling curves and X-ray data does not yet exist, the indirect evidence presented points in that direction, and has led the author to formulate the hypothesis that pure iron has no allotropic transformations below the melting point, and that its characteristic lattice structure is the body-centered cube (alpha modification). It follows as a necessary corollary to this hypothesis that the A_3 and A_4 transformations are caused by carbon and other "stranger" atoms entering the interstitial spaces of the lattice. When their amount exceeds the solubility in alpha iron for the particular temperature, they cause the iron to modify its structure in order to accommodate them.

It is hoped that investigators with proper facilities will join the author and his associates in attempts to obtain the necessary direct evidence to prove or disprove this hypothesis. The problem consists in obtaining pure iron and in proving that it is pure.

Acknowledgments

The author wishes to express his appreciation to the Westinghouse Electric & Manufacturing Co. for its liberal attitude towards research work of the nature involved in this problem and to his colleagues, particularly O. W. Ellis and N. A. Ziegler, for discussing the various phases of it with him and for valuable suggestions and information.

References

1. H. Scott: Solubility of Carbon in Alpha Iron. *Chem. & Met. Eng.* (1922) **27**, 1156.
2. J. H. Whiteley: The Solution of Cementite in α-iron and Its Precipitation. *Jnl.* Iron and Steel Inst. (1927) **116**, 293.
3. T. D. Yensen: The Magnetic Properties of the Ternary Alloys Fe-Si-C. *Trans.* A. I. E. E. (1924) **43**, 145; reviewed by Gumlich: *Elektrotech. Ztsch.* (1924) **45**, 534.
4. A. Sauveur and V. N. Krivobok: Dendritic Segregation in Iron Carbon Alloys. *Jnl.* Iron and Steel Inst. (1925) **112**, 313.
5. W. H. Hatfield: (Discussion.) *Trans.* Far. Soc. (1925) **21**, 272.
6. T. D. Yensen: Magnetic and Other Properties of Iron-silicon Alloys Melted in Vacuo. Eng. Exp. Sta., Univ. Illinois. *Bull.* 83 (1915); 27. *Trans.* A. I. E. E. (1915)**34**, 2475.
7. P. H. Brace and N. A. Ziegler: Application of a High-vacuum Induction Furnace to the Study of Gases in Metals. *Proc.* Inst. Metals Div., A. I. M. E. (1928) 544.
8. F. S. Tritton and D. Hanson: Ferrous Alloys Research. Pt. II.—Iron and Oxygen. *Jnl.* Iron and Steel Inst. (1924) **110**, 90.
9. L. Jordan and J. R. Eckman: Gases in Metals, II. The Determination of Oxygen and Hydrogen in Metals by Fusion in Vacuum. Bur. Standards *Sci. Paper* No. 514 (1925) **20**, 445.
10. Z. Jeffries and R. S. Archer: The Slip Interference Theory of the Hardening of Metals. *Chem. & Met. Eng.* (1921) **24**, 1057.

11. A. Westgren and G. Phragmén: X-ray Studies of the Crystal Structure of Steel. *Jnl.* Iron and Steel Inst. (1922) **105**, 241.
12. Ad. Fry: Stickstoff in Eisen, Stahl und Sonderstahl. Ein neues Oberflächenhartungsverfahren. *Stahl u. Eisen* (1923) **43**, 1271.
13. G. Hägg: X-ray Studies on the "Nitrides" of Iron. *Nature* (1928) **121**, 826.
14. F. Osmond: On the Critical Points of Iron and Steel. *Jnl.* Iron and Steel Inst. (1890) **37**, 62.
15. W. Gontermann: Bemerkungen zum System Eisen-silizium. *Ztsch. f. anorg. Chem.* (1908) **59**, 384.
16. G. Charpy and A. Cornu: Sur les transformations des alliges de fer et de silicium. *Comp. Rend.* (1913) **156**, 1240.
17. G. Charpy and A. Cornu-Thenard: Researches on the Iron, Silicon, and Carbon Alloys. *Jnl.* Iron and Steel Inst. (1915) **91**, 276.
18. K. Honda and T. Murakami: Structural Constitution of Iron-carbon-silicon Alloys. *Jnl.* Iron and Steel Inst. (1923) **107**, 546.
19. R. Ruer and R. Klesper: Die $\lambda\partial$-Umwandlung des reinen Eisens und ihre Beeinflussung durch Kohlenstoff, Silizium, Kobalt und Kupfer. *Ferrum* (1914) **11**, Heft 3, 257.
20. M. A. Sanfourche: Contribution a l'étude des ferro-siliciums. *Rev. de Mét.* (*Mem.*) (1919) **16**, 217.
21. F. Wever and P. Giani: Beiträge zur Kenntnis des Systems Eisen-Silizium. *Mitt.* Kaiser Wilhelm Inst. (1925) **7**, 59.
22. G. Phragmén: Constitution of the Iron-silicon Alloys. *Jnl.* Iron and Steel Inst. (1926) **114**, 397.
23. D. Hanson: The Constitution of Silicon-carbon-iron Alloys and a New Theory of the Cast Irons. *Jnl.* Iron and Steel Inst. (1927) **116**, 129.
24. P. Oberhoffer: Zur Kenntnis der Eisen-silizium Legierungen. *Stahl u. Eisen* (1924) **44**, 979.
25. N. B. Pilling and G. P. Halliwell: Critical Ranges of Iron-silicon Alloys, and Graphitization in Silicon-steel. Westinghouse Elec. & Mfg. Co. Tech. Repts. L No. 2.612 and L No. 2.614 (Jan. 28 and 29, 1924).
26. T. D. Yensen: Iron-silicon-carbon Alloys: Metallography, Magnetic Properties, Metallurgy. Westinghouse Elec. & Mfg. Co. *Sci. Paper* No. 184 (Jan. 21, 1925). Lecture delivered before joint meeting of Pittsburgh Sections of Am. Electrochem. Soc. and A. I. M. E., Jan., 1925. Most of diagrams of present paper have been taken from above paper with slight modifications.

DISCUSSION

A. Sauveur, Cambridge, Mass. (written discussion).—For lack of time, I have not been able to study Mr. Yensen's paper as carefully as its importance demands, and I may later desire to modify some of the remarks which I now offer.

The author introduces his subject with the statement that no one would be justified in assuming that pure iron has allotropic transformations for the simple reason that pure iron has not yet been made and tested. For similar reasons, it is not known whether pure iron is ductile, and still is there anyone who would hesitate to describe it as a ductile metal? Copper 100 per cent. pure has never been tested, but no one would hesitate, I believe, to say that pure copper has great electrical conductivity. The thought that copper owes its electrical conductivity to the presence of impurities could hardly be entertained. Had metallurgists been asked whether pure iron had allotropic transformations, it is not likely that any would have hesitated to reply in the affirmative. It is, of course, possible that after reading Mr. Yensen's paper some might merely hesitate.

Having found by numerous experiments that the purest iron obtainable has a marked A_3 point which, if anything, increases in intensity with increased purity, it is most logical to infer that the element iron undergoes at that temperature an allotropic transformation. The author's reason for conceiving the possibility of the absence of allotropic transformation in strictly pure iron is based on the action of silicon on iron containing very small amounts of carbon in causing the disappearance of both the A_4 and the A_3 points. It is stated on page 330 in the following words:

"If now a decrease in carbon from 0.1 to 0.01 per cent. decreases from 3 to 2 per cent. the silicon necessary to cause A_3 and A_4 to disappear, is it not logical to assume that a further decrease in carbon will further decrease the necessary silicon until in the limit with no carbon (or C less than 0.001 per cent.) no silicon is needed, provided oxygen and other interstitial impurities can be kept out?"

From this wording we naturally infer that the relation is a linear one and we then find that for zero carbon 1.89 silicon would be required.

If the relation is not a linear one but is represented as shown in Fig. 3, 4 and 5, it does not seem to me that they afford strong support of the author's views, the curves having been drawn to a great extent to fit the case. In order to account for the unexpected belief that the presence of minute proportions of impurities may be the cause of allotropic transformations of iron, the author offers some ingenious speculations which, in my opinion, are not convincing. We do not readily grasp the inference he ascribes to these impurities in causing the solvent iron to assume at a certain temperature (A_4) a form (face-centered lattice)in which they are more soluble and at a lower temperature (A_3) they return to a form (body-centered lattice) in which they are less soluble.

It is to be hoped that experts on X-ray analysis will express their opinions on these points. They will carry much more weight than what I have attempted to say. It should also be borne in mind that allotropic transformations are believed to be a property of some elements and that the possibility of an impurity inducing an allotropic transformation in an element is an entirely new conception which must pass the gauntlet of searching criticisms and experiments before it can be generally accepted.

H. W. GILLETT, Washington, D. C. (written discussion).—The Bureau of Standards naturally has been interested in pure iron, and indeed has a general continuing project for the study of the properties of pure metals. As purer metals become available, it is the policy of the Bureau to redetermine the various physical properties. While various sections of the Bureau are desirous of having pure iron for study, work on pure nickel in cooperation with the International Nickel Co., on pure thorium in cooperation with the Westinghouse Lamp Co., on pure zinc and cadmium in cooperation with the New Jersey Zinc Co. and on various pure metals of the platinum group, especially rhodium, has so occupied our attention that serious work on pure iron has not been very active.

However, in the hope of obtaining carbon-free iron, experiments were made in 1925, in which electrolytic iron was crushed, burnt in oxygen as if for carbon combustion and the oxide reduced to sponge iron by heating in hydrogen at 900° C. The charge was taken out from time to time and weighed. It was broken up as much as possible each time to give the particles free access to hydrogen, and reduction and weighing continued till no further loss in weight occurred. The product was sponge iron of clean metallic luster, caked together in a fairly solid slug, but could be readily crumbled to powder. Carbon determinations by the Chemical Division were reported "carbon not detected." Carbon present to the extent of 0.001 per cent. should have been detected.

The powder was packed into a tiny porcelain crucible which was hung from the tip of the thermocouple of the inverse rate analysis apparatus used at the Bureau.[27] Heating and cooling curves, taken *in vacuo*, run in duplicate, failed to reveal A_2 and A_3, and, of course, A_1 was absent. Slight irregularities in these curves made the apparent evidence of no transformations in iron free from carbon open to some question, and although we speculated upon the possibility of the absence of transformations, we did not consider the evidence conclusive, especially since on melting the oxidized and reduced sponge iron *in vacuo* in a zirconium silicate crucible and taking thermal analysis of solid specimen from the melt, A_2 and A_3 were clearly shown (Fig. 7*B*).

Microscopic examination showed oxide inclusions, and while no further analyses were made at that time it was evident that the material did not deserve the name "pure" iron.

By comparison with the thermal critical point curve of ordinary vacuum-fused electrolytic iron (of which the heating curve only is shown in Fig. 7*A*,) it will be seen that A_3 is fully as strong in the solid, carbonless but oxide-containing specimen.

In solid specimens from melted metal, which, so far, have always been impure as to carbon or oxygen or both, our experience is that A_3 increases in intensity as the carbon decreases. It is stronger in ordinary fused electrolytic iron than in metal of slightly higher carbon. The anomaly that the power showed no transformations while the solid metal did was not studied further at that time, though the possibility of the absence of transformations in carbonless iron was discussed with a few people and the idea kept in mind for use in future work on pure iron.

Contact of the sponge iron powder with the thermocouple in the crucible method may not have been satisfactory, although this method has been used in work at the Bureau on iron-nitrogen alloys studied in powder form and appears to reveal small thermal critical points. It is preferable, however, to briquet the powder into a compact specimen which is squeezed into contact with the thermocouple tip. The small A_2 point is often clearly shown with such briquets. The intensity of A_3 in these briquets, of powdered electrolytic iron nitrided in an ammonia-nitrogen-hydrogen mixture (but not containing enough nitrogen to make it likely that all the iron is in chemical combination with nitrogen) is greatly diminished from that of a similar un-nitrided specimen. In many cases both A_3 and A_2 are absent although small critical points at lower temperatures caused by the thermal changes in the iron-nitrogen system are clearly shown. Since oxygen is presumably removed from the electrolytic iron by the hydrogen used in the nitriding treatment, and since it is well known that carbon is similarly though more slowly removed, it is possible that the disappearance of A_3 and A_2 in these specimens may be due to the removal of carbon and oxygen.

Yensen's paper brought the subject up again, so it was decided to try thermal analysis on briquets. Another specimen of electrolytic iron that had been oxidized just as in a carbon combustion, to free it from carbon, and then reduced to constant weight by hydrogen, was briquetted under pressure of about 75,000 lb. per sq. in. and thermal analysis run *in vacuo* on the briquet. This sponge iron was made in 1925 and stored but was a different lot from that used for the 1925 thermal analysis

---

[27] G. K. Burgess: Methods of Obtaining Cooling Curves. U. S. Bur. Stds. *Sci. Paper* 99 (1908).

H. Scott and J. R. Freeman, Jr.: Use of a Modified Rosenhain Furnace for Thermal Analysis. U. S. Bur. Stds. *Sci. Paper* 348 (1919).

H. J. French: Recording Chronograph for the Inverse Rate Method of Thermal Analysis. U. S. Bur. Stds. *Tech. Paper* 230 (1923).

tests. The curves showed no transformation points for the briquets, and were similar to those shown in Fig. 7*D*.

As a check to see if the briquets gave dependable thermal curves, some ordinary electrolytic iron analyzing 0.012 per cent. C, 0.006 Si, 0.013 S, 0.70 O, 0.022 H, and 0.01 N (P was not determined but the usual P content runs 0.001 per cent. or below), was crushed and briquetted, and thermal analysis was run *in vacuo*. In a preliminary run, material 80 mesh and finer, annealed 3 hr. at 900° C. *in vacuo* to render it more readily briquetted was used. A normal A_3 point was shown, but no A_2.

The next run was made on unannealed, crushed electrolytic iron, in which the particles were over 80 mesh. By increasing the briquetting pressure a firm briquet

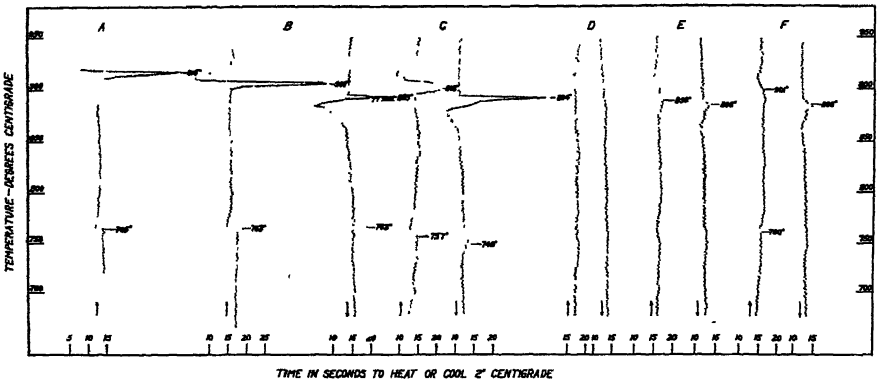


FIG. 7.—INVERSE RATE THERMAL ANALYSIS CURVES.

A—For ordinary solid electrolytic iron, vacuum fused. Heating curve only.

B—For solid, vacuum fused, *carbon-free* iron (melted *in vacuo* after oxidation and reduction). Contains oxygen, visible metallographically, amount not determined.

C—For briquetted, unfused, electrolytic iron. Contains 0.50 per cent. oxygen. Originally contained 0.012 per cent. carbon.

D—For briquetted, unfused, *carbon-free*, oxidized and reduced iron. Specimen held for 2 hr. at 975° C. before taking the cooling curve. Weight of sample, 1.61 g. Second run on same briquet. Neither run showed inversion points. Oxygen content approximately 10.5 per cent.

E—For briquetted, unfused, mixture of 0.065 g. electrolytic iron and 2.84 g. carbon-free oxidized and reduced iron. Specimen held for 2 hr. at 975° C. before taking the cooling curve.

F—For briquetted, unfused, *carbon-free* oxidized and reduced iron. Specimen held for 2 hr. at 975° C. before taking cooling curve in first run. Second run shown. Sample not held, but cooling curve taken immediately after the heating curve on the second run. Weight of sample 2.72 g. Oxygen content approximately 11.3 per cent.

was produced. The thermocouple tip was carefully brought into as firm contact with the briquet as was feasible without danger of disintegrating the briquet. This curve showed both A_2 and A_3 (Fig. 7*C*). After the run the briquet was analyzed for oxygen, nitrogen and hydrogen and 0.50 per cent. O, 0.01 per cent. N, and no hydrogen found. The drop in oxygen content corresponds closely with the oxygen equivalent as water of hydrogen that was lost. Carbon could not be determined; the thermal analysis samples weigh only about 1½ to 2½ g. and the whole sample was required for the determination of oxygen, nitrogen and hydrogen, and even the whole sample would have been insufficient for a carbon determination. The high oxygen content is normal for electrolytic iron which has not been acid-washed to remove surface oxidation. Electrolytic iron rusts rapidly in ordinary air. With this oxygen content it is a question whether much of the original carbon was left after heating to 950° C. in the high vacuum used in the thermal analysis, though it is

doubtful whether all the carbon would be removed before the specimen reached the A_3 point on the heating curve.

This briquet thus having shown the thermal points with definiteness, a run was then made on another briquet of the oxidized and reduced iron. Again neither A_2 nor A_3 appeared (Fig. 7*D*). In previous runs the specimens had been heated to about 950° C. and cooled at once, but this specimen was held for 2 hr. at 975° C., because Dr. E. W. Washburn, of the Bureau of Standards, pointed out that many cases are known, such as that of sulfur, in which a pure material fails to pass through the transformations required by the equilibrium diagram unless some catalyst is present or the equilibrium temperature is greatly exceeded. This is, however, considered to be a case of suspended transformation of the pure substance rather than of a different true equilibrium for the pure substance alone as compared to the substance in a binary system. However, the heating for 2 hr. well above the A_3 temperature either did not start the inversion, for the cooling curve was as devoid of transformations as the heating curve, or the transformation, even though it had taken place on holding at 975° C., was again suspended on cooling.

Since A_2 was not detected in the oxidized and reduced sample, it seemed desirable to look into the magnetic behavior of the material at the A_2 temperature. Specimens of both the carbonless sponge and the crushed electrolytic iron were packed into fused quartz tubes, the tubes evacuated and sealed. These samples were then examined magnetically from 20° to over 800° C. Both samples showed normal magnetic behavior at both rising and falling temperatures through the usual A_2 range. There is, of course, no necessary reason for considering that the A_2 thermal point has any relation to the magnetic behavior, and the material might have no A_2 thermal point and yet behave in a normal magnetic fashion. The apparent lack of A_2 is therefore not contradicted by the magnetic tests.

We again returned to thermal analysis, and in order to test further the idea of a "suspended transformation," recourse was had to the method of "seeding out" used long ago by Carpenter[28] in work on brass. A briquet was made up consisting of 2.84 g. of the oxidized and reduced iron and 0.066 g., or 2.25 per cent., of the ordinary crushed electrolytic iron. This corresponds to less than 0.00001 g. of carbon in the specimen; *i. e.*, less than 3 parts per million.

Thermal analysis on this briquet, which also was held at 975° C. for 2 hr., gave the curve shown in Fig. 7*E*. The magnitude of A_3 is not far from 2 per cent. of that in Fig. 7*C*; that is, one might argue that only the 0.066 g. of electrolytic iron contributed to the heat effect, and that it appears that the presence of the electrolytic iron, even though forced into close contact with the oxidized and reduced iron, did not act as a "trigger" to start transformation of the latter. That A_2 is not detectable is not surprising since detection of a point that would have only 2 per cent. of the intensity of A_2 in Fig. 7*C* would obviously be below the sensitivity of even this very sensitive method.

Up to this point all the evidence indicated that the oxidized and reduced iron could not readily be induced to show A_3. The next run, however, indicated that the matter is not so simple. Another briquet of the oxidized and reduced iron was made up, using 2.72 g. instead of 1.61 g. (which was the weight of the specimen whose thermal analysis curve is shown in Fig. 7*D*) in the hope that the increased mass of metal might favor detection of any points of small intensity.

At the bottom of the slug of sponge obtained after reduction of the oxide there was a small patch, possibly of unreduced oxide, more likely of rust. The remainder of the slug had a bright metallic appearance. The material from which the 2.72-g. specimen

[28] H. C. H. Carpenter: The Structural Resolution of the Pure Cu-Zn Beta Constituent into Alpha and Gamma. *Jnl.* Inst. Metals (1912) **8**, 51.

for thermal analysis was made was taken from the vicinity of this patch of oxide though care was taken to include no visible oxide.

The thermal analysis (Fig. 7*F*) gave an apparent heat absorption of small intensity at about the A_2 temperature, on the heating curve. After holding for 2 hr. at 975° C. the cooling curve was taken, and showed an A_3 point of about the same intensity as that in the sample of mixed special and electrolytic iron (Fig. 7*E*). A second heating curve was taken, and after this, a second cooling curve was taken at once, without holding at 975° C.

The second run gave curves which were exact duplicates of those of the first run.

It was thought that some difference in oxygen content might account for the difference between the thermal curves shown in Fig. 7*D* and *F*, so oxygen was determined on these two specimens and on the original unbriquetted oxidized and reduced iron. Knowing how readily ordinary electrolytic iron oxidizes in storage, it was expected that the reduced sponge would carry oxygen, but the analytical figures were something of a shock. They were: original sponge, 14.5 per cent.; thermal analysis specimen of Fig. 7*D*, 10.5 per cent.; thermal analysis specimen of Fig. 7*F*, 11.3 per cent. Direct determination of iron on samples of the original sponge gave 86.5 and 88 per cent. Fe, or 13.5 and 12 per cent. oxygen by difference.

If it be assumed that the oxygen is present as FeO, the specimens contained 46.5 to 64 per cent. of FeO; if as Fe_2O_3, 35 to 48 per cent. of Fe_2O_3. It is recognized that the surface of the sponge is huge in relation to the mass and that (as is so clearly brought out by Evans)[29] any iron surface exposed to air at once becomes covered with a film of oxide. Thus with very finely divided iron the percentage of oxygen bound on the surface may be very high. It is surprising that the iron was not pyrophoric and that oxidation did not go further, if it was going as far as this. Moreover, no one would guess by looking at the specimen that it was appreciably contaminated by oxide. It has a silvery appearance, sticks together when briquetted and the sample heated in an evacuated fused quartz tube in the magnetic test has sintered together under its own weight just as thoroughly as has the ordinary electrolytic iron.

That the particles were really coated with an invisible film was made clear on crumbling some of the original slug and scattering the particles on a slightly acid solution of copper sulphate. The particles floated and did not precipitate copper for several minutes, even if swirled into the solution. If a particle was crushed between the beaker and a stirring rod so as to break through the oxide film, copper was instantly precipitated upon it.

The specimens used in obtaining the curves of Figs. 7*D*, *E*, and *F* therefore are by no means to be considered as pure iron, but as iron plus much oxide. Why Fig. 7*D* shows no inversion points and Fig. 7*F* shows such weak ones is still unsolved. Certainly metallic iron was present, in as nearly carbonless a state as one can hope to attain.

If dissolved iron oxide causes the appearance of A_2 and A_3 in carbonless iron, as in the fused sample (Fig. 7*B*), why should not iron oxide, certainly in intimate contact with the iron, be dissolved in the metal after 2 hr. at 975° C. (Fig. 7*D*) and if it did dissolve why are A_2 and A_3 so weak in Fig. 7*F*? One possible explanation for the failure to detect points in the carbon-free material tested as loose powder, or as some briquets, the detection of weak ones in other briquets, and of strong ones in the fused sample, might be that the oxide film so insulated each tiny particle that, due to small temperature variations throughout the mass, each one transformed as a unit and did not have any trigger action to set off its insulated neighbors, thus spreading the transformations out so they were undetected or weak. The briquet of crushed electrolytic

[29] U. R. Evans: The Passivity of Metals and Its Relation to Problems of Corrosion. *Trans.*, A. I. M. E. (1929) Inst. Metals Div., 7.

iron contained much larger grains and much less oxide, so there was more metal-to-metal contact. Differences in briquetting pressure may thus be considered as a possible cause for the difference between Figs. 7*D* and *F*.

These experiments do not by any means show whether Yensen's hypothesis that there are no inversion points in pure iron is correct or not, because the irons used were far from pure. They do, however, indicate that A_2 and A_3 may be vastly reduced in intensity, if not entirely absent, in carbonless iron even though it be mixed with oxide, so that Yensen's hypothesis deserves a respectful hearing. Certainly after the questions Yensen has raised it is plain that the term "pure iron," so often used,[30] has been loosely used, and that the actual oxygen content as well as the actual carbon content of any material so described will have to be determined before experiments on so-called "pure iron" can be accepted as relating to the pure metal and not to a binary or ternary system in which the other components are present in unknown quantities. It is doubtful whether much of the so-called "pure" vacuum-melted electrolytic iron used contains less than 0.003 per cent. C and 0.005 per cent. O. If Yensen has, as he says, been able to strike a balance on one melt that eliminates both, thermal analysis curves on this lot would be most interesting.

I am indebted to Louis Jordan for preparation of the iron samples, to H. C. Cross for thermal analyses, to H. C. Vacher for the oxygen determinations and to R. L. Sanford for the magnetic tests.

Incidentally, it is incorrectly stated in Yensen's paper (page 324) that work by Jordan and Eckman at the Bureau indicates that the solubility of oxygen in iron is 0.02 to 0.05 per cent. at 20° C. and 0.20 per cent. at 1530° C. Analyses for total oxygen tell nothing about the state of the oxygen, and no such conclusion was drawn as to solubility at 20° C. Metallographic evidence makes us sure that it is much lower than the figures given. Tritton and Hanson do state that the solid solubility is estimated to be about 0.05 per cent. oxygen, but the Bureau of Standards has not so stated. The figure for solubility at 1530° C. is a rough one, recorded in *Chem. & Met. Eng.* (1922) **26**, 778.

A. Hayes, Middletown, Ohio (written discussion).—In the theory of solutions, we have what is known as the laws of the dilute solution, in which it is assumed that the activity, such as, for example, the vapor pressure of the solute is proportional to its mol fraction, also in this dilute solution the activity of the solvent is similarly proportional to its mol fraction and the change in the activity of the solvent is proportional to the mol fraction of the solute.

If you should assume, as I believe you have in your discussion, that the A_3 point is at 905° C. in iron contaminated by oxygen, the position of the A_3 transition in pure iron free from oxygen, as well as all other contaminating constituents, should be obtained by extrapolating the A_3 line. The same thing should hold for the A_4 line. In making such an extrapolation, however, we did not use the slope of the A_3 line as obtained by plotting temperature of the transition against per cent. by weight of carbon, but rather would we plot the A_3 line by using temperature as one coordinate and the mol fraction of carbon in the mix as abscissas. We have equation

$$\frac{dT}{dx} = (K-1)\frac{RT^2}{\Delta H} \qquad [1]$$

---

[30] G. K. Burgess and J. J. Crowe: The Critical Ranges A_2 and A_3 of Pure Iron. *Trans.*, A. I. M. E. (1914) **47**, 665.

J. R. Cain, E. Schramm and H. E. Cleaves: Preparation of Pure Iron and Iron-carbon Alloy. U. S. Bur. Stds. *Sci. Paper* 266 (1916).

A. Sauveur and C. H. Chou: The Gamma-alpha Transformation in Pure Iron. See page 350.

in which T is the absolute temperature, X is the mol fraction of the solute, R is the ordinary gas constant in the ideal gas equation, ΔH is the heat effect for the transition of, in this case, alpha iron into gamma iron, or of gamma iron into delta iron, as the case may be; while K is the distribution coefficient of the solute which might be oxygen, nitrogen or silicon; in fact, any other solute you please to consider.

For example, suppose we consider carbon as the solute. K is the concentration of carbon in alpha iron at the transition temperature over the concentration of carbon in gamma iron. In this case, since carbon is almost immiscible in alpha iron, the value of K is very small, and this equation takes the form of

$$\frac{dT}{dx} = \frac{RT^2}{\Delta H} \qquad [2]$$

For small variations in temperature, equations 1 and 2 may be integrated directly, considering $\frac{RT^2}{\Delta H}$ a constant, as well as considering K a constant in equation 1. Using as limits 0 to X for the solute gives

$$\Delta T = (K-1)\frac{RT^2}{\Delta H} \cdot X \qquad [3]$$

and equation 3 gives

$$\Delta T = \frac{RT^2}{\Delta H} \cdot X. \qquad [4]$$

Equation 4 is the well-known one for lowering freezing point for the condition of pure solvent separating from the solution. Equation 1 has a broader application in that the constant K enables us to apply this equation to solutes with various distribution coefficients between the two allotropic forms. For an element like silicon, for example (most investigators believe silicon more soluble in alpha than in gamma iron), K is considerably greater than unity, which means that silicon is more soluble in alpha iron at the transition temperature than it is in gamma iron. On this account silicon raises the temperature of the A_3 transition. If equation 1 is applied to the gamma delta transition for silicon as the solute, K is less than 1, silicon being more soluble in delta than it is in gamma iron, and as a result the temperature of the gamma delta transition is lowered by additions of silicon.

Application of equation 1 to the alpha gamma transformation and to the gamma delta transformation shows that for a solute like silicon the A_3 and A_4 lines are diverging as we approach more nearly pure solvent. Thus we would not expect to find A_4 and A_3 ever merging into a single point for solutes of the type of silicon as purer iron is approached.

On the other hand, for solutes similar to carbon with respect to distribution coefficient, the A_3 and A_4 lines are converging and were the slope of there lines such that with the mol fractions of impurities, such as oxygen, nitrogen, etc., of sufficient magnitude so that the slopes of the A_3 and A_4 lines in the neighborhood of dilute solutions would be sufficient to bring about the intersection of these lines at 0 concentration of all solutes, we would expect to find the allotropic transformations A_3 and A_4 eliminated in pure iron.

It may be said that the laws of the ideal solution are approached in all liquid and solid solutions that have been investigated as the concentration of the solute approaches 0, and that the equations quoted herein are based on the second law of thermodynamics, together with the laws of the ideal solution. If we consider solutes of the class similar to silicon with respect to distribution coefficient, and again consider solutes of the class of carbon with respect to distribution coefficient, the application of these equations leads to the conclusion that it is only with solutes of the class similar to carbon that we should ever expect to find intersection of the A_4 and A_3 lines. Consequently, it would seem that if we were to make the assumption that the

sum of the mol fractions of all impurities present in the purer irons that have been manufactured behave like carbon with respect to distribution coefficient (in other words, behave in such a manner as to make equation 4 strictly applicable); if, then, we were to apply this equation to the sums of the mol fractions of all impurities present in the purest irons that have been manufactured, and if we should find in such an application of equation 4 that A_4 and A_3 do not intersect, it could be rather safely concluded that A_3 and A_4 will not intersect under any conditions in the neighborhood of pure iron, because the rate at which the A_4 and A_3 lines converge is at a maximum when we assume solutes all like carbon; that is, solutes completely immiscible in the alpha and delta modifications.

In equation 4 all of the quantities, except X the mol fraction of the solute, on the right-hand side of equation are either constants or are characteristics of the solvent only, which is iron. For example, ΔH may be shown to be the heat of transformation of alpha into gamma iron. T, as was stated earlier, is the absolute temperature of the alpha-gamma transition in pure iron, and R is the well-known gas constant. Such a consideration shows that the quantity $\frac{RT^2}{\Delta H}$ is a constant, whose value is determined by the characteristics of the solvent, and should therefore be independent of the nature of the solute, providing values of X be limited to small enough values so that the laws of ideal solutions will be approached. If such is the case, by making the assumption that would allow the greatest opportunity for intersection of the A_3 and A_4 lines as conditions of pure iron are approached—that is, that all impurities are soluble in the gamma phase, and are completely insoluble in the alpha phase—X may be considered the sum of the mol fractions of all such impurities. By use of equation 4 and by reading values off of the A_3 line for temperature and mol fraction of carbon, the heat of transition from alpha to gamma iron may be calculated, and such a calculation does check approximately calometric determinations. What this indicates is that the laws of dilute solutions are approximated, although somewhat roughly, by carbon as the solute in gamma iron.

Numerical Values Used in the Preceding Suggested Extrapolations

As a numerical illustration of the nearness of approach that might be expected in extrapolating the A_3 line to pure iron, we have used equation 5, taking the following numerical values:

$$X_c = X_1 = 0.014$$

the mol fraction of carbon in a pure iron-carbon alloy containing 0.3 per cent. carbon alloy by weight, and in which is assumed a negligible mol fraction of oxygen.

$$X_c + X_0 = 0.00256$$

in an iron-carbon alloy containing 0.01 per cent. carbon by weight, and in which the oxygen concentration is assumed to be 0.06 per cent. by weight.

$$T_1 = 900° \text{ C. or } 1173° \text{ Abs.}$$

and is taken from the iron-carbon diagram of the International Critical Tables.

$$T_2 = 834° \text{ C. or } 1107° \text{ Abs.}$$

When these values are substituted in equation 5, a value of 446 cal. is obtained for ΔH, the molal heat of transformation of alpha iron to gamma iron in this temperature interval, or a value of 7.98 cal. per gram for this transition.

The extrapolations were made using equation 5

$$\frac{1}{T_2} - \frac{1}{T_1} = \frac{4.56}{446} \log \frac{1 - X_1}{1 - X_2} = 0.01022 \log \frac{1 - X_1}{1 - X_2}$$

and taking $X_2 = 0.014$, which corresponds to the mol fraction of solute in the 0.3 per cent. carbon alloy, and taking $X_1 = 0$ with the corresponding value of 1107° Abs.

for T_2 to calculate T_1. A value for T_1, the temperature of the A_3 transition in pure iron, should result if the only impurity other than carbon in the alloy was oxygen.

With such a calculation the absolute temperature of the A_3 transition in pure iron should be 1195° Abs. or 922° C., which is only 22° higher than we obtain if we neglect oxygen as an impurity.

Consideration of equation 1 as applied to the A_4 line offers a greater possibility of the explanation of an intersection of the A_3 and A_4 lines than does the application of equation 5 to the A_3 line.

First the fact that if the solutes, carbon and iron oxide, have a considerable solubility in gamma iron and an almost negligible solubility in delta iron, K is very large, and the slope of the A_4 line would also be very large. If the solubilities of these solutes in delta iron were zero, this slope would be infinite, or, in other words, parallel with the temperature axis.

This discussion, from the standpoint of equations 1, 2, 3, 4, and 5 is as fundamental as are the laws of thermodynamics and cannot well be questioned. If, however, pure iron has no A_3 or A_4 transitions, the significance of these equations and this experimental fact of intersection of the A_3 and A_4 lines must be that the data upon which the A_4 line is drawn is not accurate, and that its slope is considerably greater than has been thought.

Therefore I believe that considering the relative accuracy with which the A_3 and A_4 lines are located, an explanation of such an intersection, if it exists, will be found in errors in the position and slope of the A_4 line rather than in that of the A_3 line.

I am frank to state that had not Dr. Gillett interjected his rather startling confirmation of Dr. Yensen's thesis, my discussion would have been much more positively adverse than it is. I shall await with the greatest interest the outcome of this investigation.

R. H. Aborn, Cambridge, Mass. (written discussion).—Although the criteria of relative strengths of combination and diffusion forces in differentiating intermetallic compounds from solid solutions may be entirely valid, their application is rather vague and the whole conception is largely speculative. On the other hand, the definitions proposed by Westgren and Phagmén that in an ideal solid solution all atoms are structurally equivalent while in an ideal intermetallic compound only chemically identical atoms can be structurally equivalent, form a clear-cut working basis for differentiation. Thus in the iron-nickel system all X-ray investigations point to the structural equivalence of all the atoms (*i. e.*, the solute is substituted in a completely random manner on the solvent lattice, which may in this case be body-centered cubic or face-centered cubic, according to the total composition). In the iron-silicon system, however, beyond the range of solid solution of silicon in the alpha iron lattice, the compounds FeSi and $FeSi_2$ are successively formed. In each of these the iron atoms are located in a certain set of positions on a complex cubic or tetragonal lattice, respectively, while the silicon atoms lie in other positions which are structurally inequivalent with respect to the positions of the iron atoms, and the two cannot be interchanged.

It is true, of course, that there are in a number of metallic systems complex solid solutions which form intermediate stages between the ideal solution and the ideal compound, but this in no way weakens the general proposition since they can be classified according to their characteristics as inclining toward one or the other of the two types.

In regard to the interstitial elements C, N, and O, the most generally accepted effective atomic radii for these elements place them with decreasing size in the order named, the radius of N being 8 per cent. less and the radius of O being over 20 per cent. less than that of C.

The author places considerable emphasis on the deoxidizing power of silicon and says "if oxygen is partly responsible for the A_3-A_4 transformations, the removal of O by silicon should consequently tend to eliminate them." And, of course, silicon does do this, giving the "closed gamma loop" when more than 2 to 3 per cent. is present. Tin is a notoriously poor deoxidizer, yet it also closes the gamma range when more than 2 per cent. is present. The same result occurs when relatively small percentages of tungsten or molybdenum (also poor deoxidizers) are added to iron.

Mr. Yensen does develop some very interesting evidence for the non-allotropy of pure iron. Its chief value, however, as the author points out, will be to stimulate further research on the purest obtainable iron.

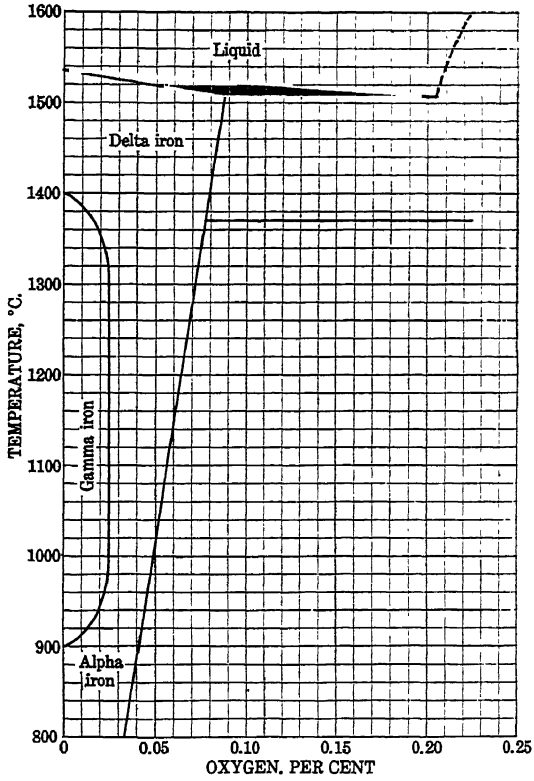


FIG. 8.—ONE CONCEPT OF SYSTEM IRON-OXYGEN (OBERHOFFER ET AL.).

G. R. FITTERER, Pittsburgh, Pa. (written discussion).—As stated by the author, one of the purposes of this paper is to encourage argument leading to the establishment of a more fundamental concept of allotropic transformations of pure iron. Unfortunately the most fundamental concepts are the least definable and it is therefore difficult to answer his challange quickly and accurately. Also, when replying to his statements one should not assume that pure iron does or does not undergo allotropic changes but seek plausible explanations, pro and con.

One bit of evidence which I would like to present deals directly with the effect of oxygen upon these transformations. The accompanying figure (Fig. 8) given by Oberhoffer[31] represents one concept of the system iron-oxygen. It is readily seen that

[31] *Stahl und Eisen* (1927) **47**, 1521.

iron containing more than 0.025 per cent. oxygen can be without allotropic transformations. Furthermore, Mr. Yensen says that "the purest iron obtainable contains a relatively large amount of oxygen, which may be responsible for the A_3 and A_4 transformation." He admits that little is known about the iron-oxygen alloys containing from 0.00 to 0.10 per cent. oxygen.

Apparently Mr. Yensen did not experiment with iron-oxygen alloys of this type but merely theorized. However, Dr. Gillett cited an instance in which no transformations were found in a sample of iron prepared by oxidizing electrolytic iron (thereby elminating carbon, phosphorus and sulfur and then reducing the oxide in a stream of hydrogen. On the other hand, Dr. Gillett pointed out that the oxygen content of the resulting sample was not known. It is quite possible that the oxygen content was within the range of no transformation in the figure.

If any research is to be done regarding transformations in pure iron it seems only fitting that it should be started with an accurate determination of the system iron-oxygen, since Mr. Yensen has made it a major issue and since this diagram is a contrary bit of evidence.

J. ALEXANDER, New York, N. Y. (written discussion).—I query whether Dr. Yensen may not have produced gamma iron under conditions which maintained it in a metastable state, and whether a sharp shock as with the supersonic waves of Loomis and Wood, or innoculation with alpha iron (for instance, by touching the hot mass with alpha iron or seeding it with alpha iron), would not determine the allotropic change. Many analogous cases are well known to chemists and physicists.

YAP CHU-PHAY, New York, N. Y. (written discussion).—This paper deals with an interesting question originally raised by Weaver, whether or not absolutely pure iron shows allotropic transformations, and Dr. Yensen is to be congratulated for his significant paper. Nevertheless, there are certain exceptions that may be taken in regard to his analysis of solid solubility and his proposed equilibrium diagram.

Let us take up first the question: "Has pure iron allotropic modifications?" No discussion of allotropic transformation is adequate without reference to the theories of Smits and Cohen. Dr. Yensen's discussions, in metallurgical language, run along parallel lines to the essential framework of Smits' theory. Accordingly, the writer is inclined to agree with him in expecting the tremendous role played by impurities, acting as catalyst insuring the constant and rapid production of internal equilibrium of the different molecular complexities of species. The work of Professor Baker on boiling points of liquids and on the melting points of solids dehydrated for a period of time extending from 9 years up throws considerable light on the effect of minute amounts of water (that is, impurity in this case) on our physical constants. Thus, he found that the boiling points of bromine, ethyl and methyl alcohols, to name but three, were raised from 63°, 78.5° and 66° C. to 118°, 138° and 120° C. respectively, and the melting points of rhombic sulfur and iodine were raised from 112° and 114° to 117.5° and 116.2° respectively. In the case of liquids, Baker came to the conclusion that this phenomenon is due to associated molecules. We should expect the melting point of iron to be higher than 1528° C.

There is considerable inferential evidence that crystal forms are governed by the configuration of the electron shells of the atoms. If one studies the periodic chart (compiled by Dr. Hubbard) one is struck by the repetition of crystal habits in the different periods. Thus Thompson, among others, suggests that the allotropy of iron may be due to the different distribution of the electrons, namely, alpha-delta, 2.12.10.2 and gamma, 2.12.9.3 electrons, the former being the more stable shell. The presence of alien atoms "binding" some of the electrons causes a disturbance in the inner equilibrium of iron, so that the atoms gradually change over to the second type

of shell. It may be assumed that this transformation is a progressive one, so that at 1400° C. a sufficient number of atoms have transformed themselves to shift the balance of the reaction in the direction of a complete change. At 900° C., the iron becomes unstable again and it then reverts to the 2.12.10.2 type of shell. This is in accordance with Tammann's Rule of Successive Transformations. The question might then be asked: "Why is the body-centered cubic configuration stable up to 1400° C. and then again at 900° C.?" We can only answer this question *a posteriori*, by saying that the stability of the second type of electron shell is limited. Perhaps the key to the explanation may be found in the so-called beta transformation. Undoubtedly the alpha iron, between 900° C. up to the point when the so-called beta transformation is observed, is somewhat unstable, this unstability being counteracted by some change (nonphasial) within the atom itself at about 760° C. It is not unlikely that in the future we may find other transformations as we decrease the temperature to absolute zero.

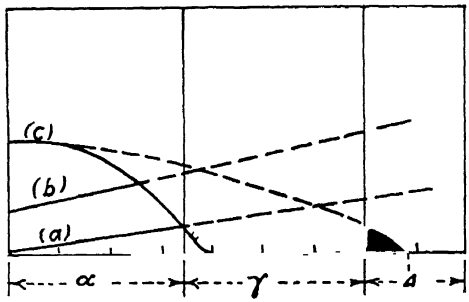


FIG. 9.—*a*. SOLUBILITY OF CARBON. *b*. CHANGE IN LATTICE PARAMETER WITH TEMPERATURE. *c*. CHANGE IN FERROMAGNETISM WITH TEMPERATURE.

There is considerable evidence that the properties of delta iron so abruptly interrupted at 1400° C. are renewed at 900° C. when the gamma to alpha transformation takes place. Thus Tamura found that the solubility of carbon in alpha-delta iron is a straight-line function (Fig. 9). Our meager data on the expansion of the lattice parameter of the delta and alpha phases also suggest a straight-line function. Dr. Honda has also shown that in a low field intensity (*b*) the loss of ferromagnetism is a gradual one and is resumed at 1400° C. when the gamma to delta transformation takes place.

In regard to the second question as to whether or not we should modify the equilibrium diagram, I am inclined to the opinion that it is not necessary at the present time. Equilibrium diagrams are themselves only approximate graphic representations of equilibria among the phases, without regard to the molecular complexities of the individual phases; that is, we consider all phases or elements as unary in behavior. When we see an equilibrium diagram of Fe and C (or Fe_3C) we mean ordinary iron and ordinary carbon. To add such refinements to the equilibrium diagram as to show the lack of allotropy in absolutely pure iron when we do not know whether there is such a thing as pure iron is like weighing a chemical sample to the sixth decimal point when our apparatus and the purity of our chemical is only good to two decimal places. However, the line showing the limited solubility of carbon in ferrite is more necessary because it comes within ordinary laboratory and practical investigations and in the future it is likely to be an important key to the explanation of many of the peculiar behaviors of iron and steels; *e. g.*, cementation, spheroidization, temper-brittleness, etc. Fig. 10 seems to me to be more consistent with the known facts. Thus, we should expect a higher melting point, a wider range of stability of the delta

phase and narrower range of stability of the gamma phase and the elevation of the A_3 point. Although conventionally we consider the critical points to take place at temperature T, in reality it is within $T + dt$. The diagram is exaggerated to show the phasial equilibria more clearly on a large scale.

It is hardly possible to prove or disprove the absence of allotropy in pure iron, because we have no methods of adequately and completely proving that our iron is absolutely pure of foreign atoms in its interstices. The problem can be attacked with more profit by thermodynamic methods. However, if we are able to produce iron of the purity, say, 99.9995 per cent., we may not find the A_3 point at 900° C., but at a much higher temperature. Also, the technique of measuring this critical temperature has to be modified because it is probable that if the heating or cooling of the specimen is rapid, we will be unable to detect the heat effect on account of the hysteresis. We should expect abnormal hysteresis in the transformations of pure elements, as the catalytic impurities are present in only a minute quantity. I shall conclude with the question: "Is allotropy not absent in all pure substances, if we know how to prepare them?"

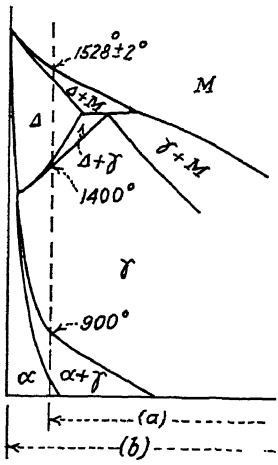


FIG. 10.—*a*. ORDINARY FE-C DIAGRAM. *b*. PURE FE-C DIAGRAM.

T. D. YENSEN (written discussion).—The author appreciates the interest taken in the paper. It has brought out, as he had hoped, some hitherto unpublished information that is stimulating and other data may appear in the periodical literature. Constructive criticism has also been offered from authorities on the subject, analyzing the problem both from a theoretical and experimental point of view, all of which is aiding in placing it on a firm foundation for further study.

There are a few points that evidently were not made clear in the paper and perhaps should be given further consideration. Dr. Sauveur, for example, thinks he is justified in extrapolating from present accepted data on iron in order to obtain the properties and characteristics of pure iron, leading to the conclusion that pure iron is ductile, that it has a certain electrical conductivity and passes through allotropic transformation points at about 900° and 1400°. On the same basis, he would believe, with Dr. Honda,[32] that the magnetic hysteresis loss of pure iron is about 2000 ergs per cu. cm. per cycle for B = 10,000 gausses, and its magnetic permeability about 8000, because these are the values obtained by extrapolation of the usually accepted data on iron-carbon alloys. Now it happens that we have reliable data on the magnetic properties of iron with very small amounts of impurities, showing that the conclusions based on such extrapolations are wrong. We have obtained actual experimental results with ring samples tested according to the most approved methods, which show a hysteresis loss less than 300 and a maximum permeability of over 60,000—one-seventh and seven times respectively what previous extrapolations would have led to. The author has shown that this is due to a previously unknown condition; namely, that carbon remains in solid solution at room temperature even after very slow cooling (see Fig. 1). Extrapolation, based on this new evidence, leads to zero hysteresis and infinite permeability for zero carbon, *provided other impurities can be kept out.* The chief difficulty is to keep oxygen out when carbon is eliminated, as oxygen has a high affinity for iron and has a solubility of the same order of magnitude as carbon.

[32] Letter to the author.

According to experimental evidence, oxygen and carbon have similar effect on the magnetic properties of iron.

It was this evidence, coupled with the fact that small amounts (1.5 to 2.5 per cent.) of substitution elements, like silicon, simultaneously eliminate the oxygen and the transformation points and greatly improve the magnetic properties, that led the author to the opinion expressed in the paper that pure iron may be free from allotropic transformations.

Our evidence in regard to ductility also leads us to believe that pure iron not only is ductile but is far more ductile than we used to think. Dr. Sauveur's statement in regard to copper seems strange, inasmuch as he surely knows that the electrical conductivity of copper is greatly affected by impurities just as the electrical conductivity and the magnetic permeability of iron are both affected by impurities.

The dash and dot curves of Figs. 3, 4 and 5 should, as stated in the paper, be regarded only as indications of what the actual curves may be like. To use them as a basis for numerical calculations is like using qualitative statements for extrapœation.

If the author's explanation is not satisfactory as to why iron, in the presence of interstitial impurities, should assume the body-centered cubic form when it crystallizes from the liquid, then change to the face-centered form at about 1400°, in which the impurities are more soluble, and finally back to the body-centered form at about 900° when it crystallizes from austenite, the explanation offered by Mr. Yap in his discussion may be more acceptable, although in the final analyses the two explanations may coincide.

Dr. Sauveur points to the current opinion that the allotropic transformations of iron is an inherent property of the element, iron, and that its existence is independent of the impurities present in the iron. It should be made clear that it is this current belief that the author is challenging. At present we have no conclusive experimental evidence one way or the other. The author is of the opinion that the transformations are induced by interstitial impurities, which we have so far been unable to eliminate simultaneously. Dr. Sauveur and many others do not agree with this view. Only time and painstaking work will disclose the truth.

Dr. Gillett's contribution as first presented appeared to confirm the author's hypothesis, and was very acceptable in that it helped to create interest in the subject even though the results could not be regarded as conclusive.

We have for some time regarded hydrogen as an ineffective deoxidizer of iron oxide, and it is presumed that the work done at the U. S. Bureau of Standards on determination of oxygen in iron has led Dr. Gillett and his associates to the same opinion. It was therefore not to be expected that completely reduced iron could be obtained by the method used. That the oxygen content should prove to be over 10 per cent., however, was a decided shock and must be due partly to oxidation during storing. The absence of transformation points for such samples may very well, as suggested, be due to the fineness of the particles and the oxide films, preventing all of them from transforming in unison.

Of more interest than the result on reduced sponge iron is the result obtained with powdered and briquetted electrolytic iron, treated with an ammonia-nitrogen-hydrogen mixture. That the untreated briquettes give definite A_3 points, while the treated ones give much diminished, or even no indications of A_3 points, seems like good evidence that pure iron may have no transformation points.

As to the suggestion that we try thermal curves on the sample for which we obtained very low carbon and oxygen, this was done some time ago. The result is a striking illustration of the sensitivity of the material to contaminating influences. Ring samples, 2.5 cm. dia., from this sample originally had permeabilities of 46,000 and 61,000. In order to make thermal tests a part of the original forging was further forged to 1.5 cm. dia. and thermal test pieces and rings about 1 cm. dia. were made.

The rings were vacuum-annealed as usual and heating and cooling curves obtained for the special test pieces, the heating being done in vacuum (0.001 mm. Hg). The usual A_3 and A_2 points were observed. But the rings gave a maximum permeability of only 25,000 and microanalysis revealed plenty of oxide inclusions in the thermal sample. Something had evidently happened to the iron, since it was first made. Furthermore, the original rings, having permeabilities of 46,000 and 61,000 when first tested, showed a decrease of about 10 per cent. when retested after having been stored under atmospheric conditions for about three months. In other words, large changes in the physical properties of iron take place at room temperature. It is not improbable that these changes are due to a gradual dissolving of atmospheric elements in the iron, and we are now in the midst of investigating this phase of the problem.

It is thus becoming increasingly evident that the problem of obtaining the properties of pure iron is difficult, and that we can arrive at them only by asymptotic methods.

The author agrees with Dr. Hayes that any hypothesis must, as far as possible, be in agreement with the accepted laws of thermodynamics and physical chemistry. There is no reason to believe that the laws of dilute solutions, for example, should not hold for the case under consideration and it would be logical to use this law as done by Dr. Hayes, for the problem of extrapolating to zero mol fraction of impurities. The big problem, however, is to obtain reliable data to use for this extrapolation.

One question, of which the settlement would greatly help in the further study of allotropy in iron, is this: Is the increase in the A_3 point with Si due to a greater solubility of Si in alpha than in gamma iron, as assumed by Dr. Hayes in his discussion? Or, is the increase due to the elimination of oxygen from solid solution by Si, in accordance with the author's present view? R. H. Aborn points out that tin, tungsten and molybdenum also close the "gamma loop" and that these are poor deoxidizers, implying thereby that removal of oxygen may not be the cause of the elimination of the A_3 and A_4 points. It might be added that the following elements, all more or less good deoxidizers, are believed to close the gamma range: aluminum, antimony, arsenic, phosphorus, titanium, vanadium.

The author appreciates the correction by Mr. Aborn as to the relative size of the carbon, nitrogen and oxygen atoms. The present opinion, contrary to that previously prevailing, places the oxygen atom at the lower end. If this is confirmed, the rate of diffusion of the oxygen atom should be greater than that of the carbon atom.

Mr. Fitterer refers to one of the three iron-oxygen diagrams suggested by Oberhoffer and his colleagues, having a "closed gamma loop." The oxygen content required to eliminate the A_3-A_4 transformations according to this diagram is 0.025 per cent. Mr. Fitterer presents this as a bit of evidence that perhaps oxygen may eliminate the transformations rather than be the cause of them. The author can not agree with Mr. Fitterer in this respect. In the first place, Oberhoffer et al do not claim that the diagram mentioned is correct, and the other two diagrams do not contain the "closed gamma loop." It is a suggestion, just as the present author's Fe-C diagram is a suggestion. In the second place, it is doubtful whether the samples of "pure" iron hitherto used in A_3 determinations contain less than 0.025 per cent-oxygen, and yet every one of them has shown A_3 transformation points. Furthermore, Tritton and Hanson found A_3 transformations in all their samples, going up to 0.21 per cent. oxygen. In view of this evidence it is difficult to see how any credence can be attached to the diagram of Oberhoffer et al.

The author agrees with Mr. Fitterer that it is most important in this connection to determine accurately the iron-oxygen equilibrium diagram, but before this can be done a reliable method of oxygen determination is essential, accurate to ± 0.001 per cent. This problem is being vigorously investigated at present, using as a basis the vacuum-graphite crucible method.

Mr. Yap's reference to the "so-called beta transformation" is, in the author's opinion, unwarranted. Disappearance of ferromagnetism at the A_2 point can be explained on the basis of kinetic theory, as done by Weiss, according to which the change should be gradual, and it is not necessary to introduce any assumption as to change in crystal structure. As X-ray evidence has shown that there is no such change, it would seem preferable to adhere to the Weiss theory, until we obtain evidence to the contrary.

Mr. Yap's contention that it is unnecessary to show lack of allotropy in pure iron, even if it could be proved, may be justified from a present practical point of view, but certainly not from a scientific point of view, and this is what we are chiefly concerned with here. Most scientists working in this field are probably very much interested to know whether pure metals exhibit allotropic transformations and the question may have an important bearing on practical problems in the future.

The Gamma-alpha Transformation in Pure Iron

By Albert Sauveur*, Cambridge, Mass., and C. H. Chou,† Lorain, Ohio

(New York Meeting, February, 1929)

The senior author of this paper has expressed the belief that when gamma iron transforms into alpha iron on reaching the A_3 point, each gamma grain does not change bodily into one or more alpha grains but that the alpha phase forms first at the boundaries and along the crystallographic planes of the austenite grains.[1] To quote:

On cooling through the point A_3, at about 900° C., iron passes from the gamma condition to a new allotropic form generally designated as alpha. This transformation, however, is not instantaneous. There are good reasons for believing that it

Fig. 1.—Schematic illustration of Widmanstättian type of structure assumed by pure iron in passing from its gamma to its alpha condition.[2]

begins at the grain boundaries and along the octahedral planes of the crystals and that it progresses until each grain of gamma iron is changed into a grain of alpha iron, the resulting structure being similar to that of gamma iron. Were it possible to retain

* Gordon McKay Professor of Metallurgy and Metallography at Harvard University.

† National Tube Co.

[1] A. Sauveur: The Widmanstättian Structure of Iron Alloys. *Proc.* Am. Philosophical Soc. (1927) **66**, 267.

[2] Fig. 1 is reproduced from paper cited in reference No. 1.

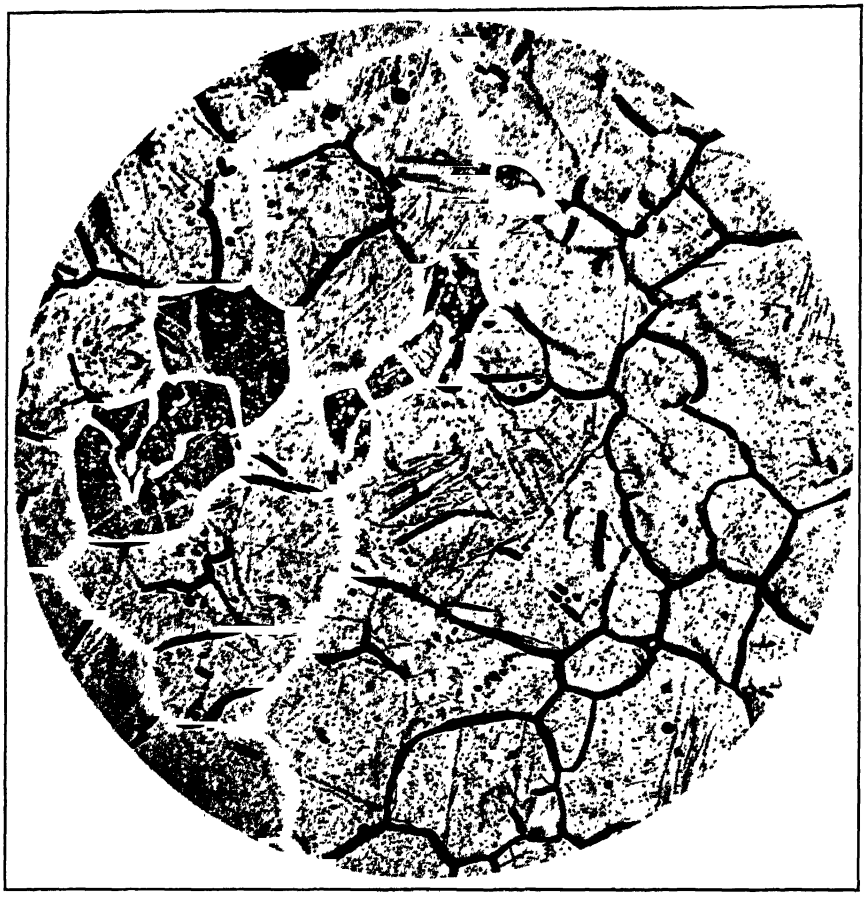


FIG. 2.—STRUCTURE OF POLISHED SURFACE OF ELECTROLYTIC IRON HEATED 2 HR. IN VACUUM TO 1000° C. AND QUENCHED IN LIQUID AIR WITH TUBE IN WHICH IT WAS HEATED. × 100.

at room temperature pure iron but partially transformed, it seems probable that a Widmanstättian structure, or rather, as later explained, a martensitic structure would be observed (Fig. 1), consisting of alpha iron at the boundaries and at the octahedral planes, and of a groundmass of gamma iron.

In order to confirm, if possible, the accuracy of that view, a number of experiments were conducted. Polished samples of electrolytic iron were heated in a vacuum, maintained in the gamma range for several hours and quenched in different media. It was hoped by such means to produce and retain on the polished surfaces a pattern which would reveal the mechanism of the allotropic transformation.

The samples were placed in evacuated quartz tubes, heated to 1000° C. and held 2 hr. at that temperature. The tubes were then immersed in the quenching bath.

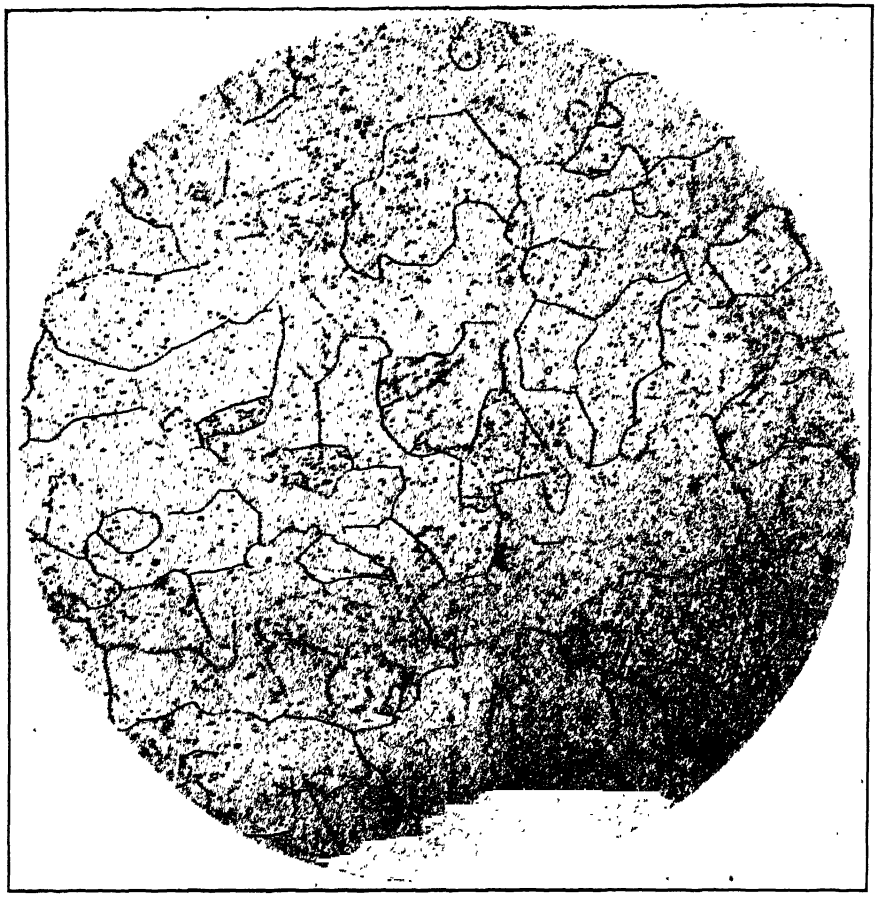


FIG. 3.—STRUCTURE OF SAMPLE SHOWN IN FIG. 2 AFTER SLIGHT POLISHING AND ETCHING WITH 5 PER CENT. NITAL. × 100.

Iced brine and liquid air were used first. The polyhedral austenitic structure existing at the time of immersion was very clearly revealed (Fig. 2). This is generally ascribed to iron volatilizing at the grain boundaries.

After slight polishing and etching, the normal alpha-grain structure was revealed below the surface (Fig. 3). The internal structure of the grains (Fig. 2), while in some instances suggesting a martensitic pattern, was not fully conclusive. The cooling had not been drastic enough, even in liquid air, possibly because of failure to bring the sample in direct contact with the quenching liquid, the vacuum surrounding them retarding their cooling.

Recourse was then had to mercury and the highly satisfactory results shown in Figs. 4 to 8 were obtained. It seems evident that the mechanism of the allotropic transformation of gamma into alpha iron is

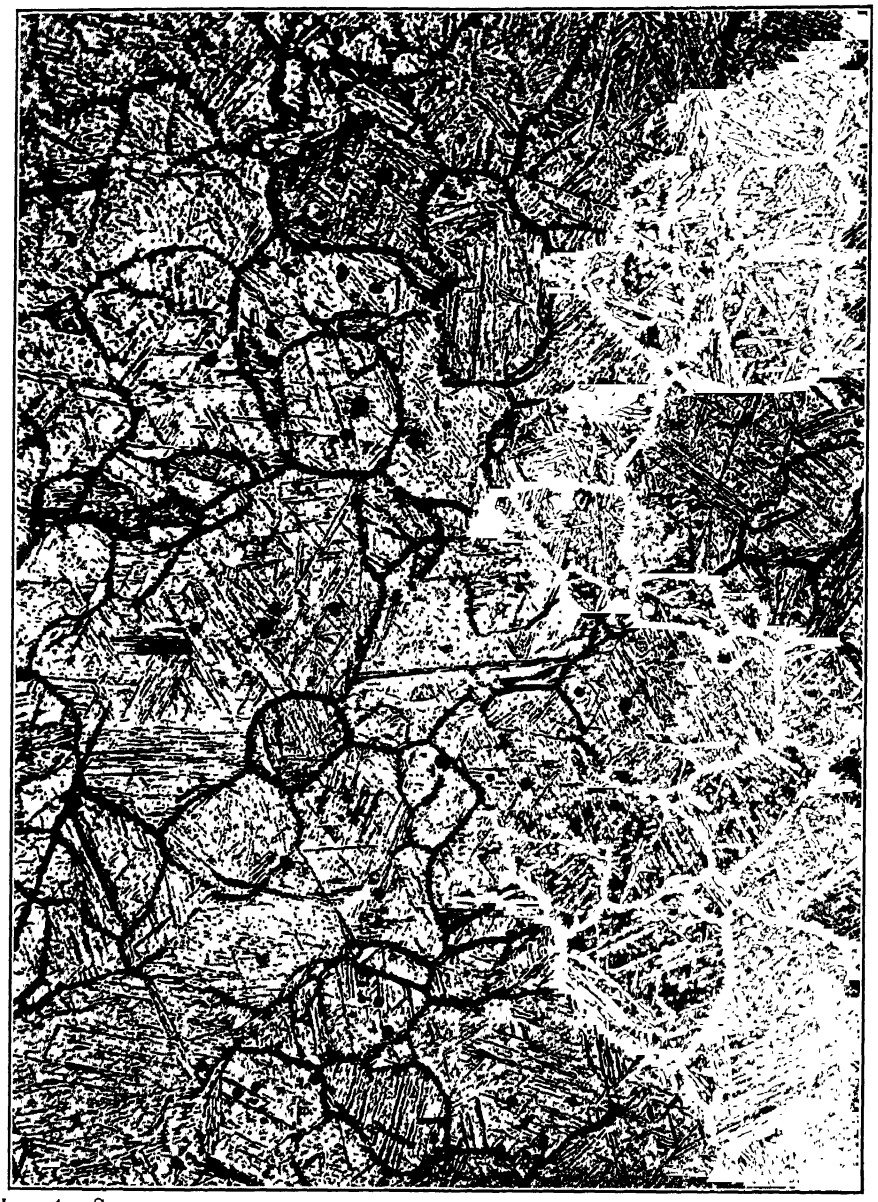


FIG. 4.—STRUCTURE OF POLISHED SURFACE OF ELECTROLYTIC IRON HEATED 2 HR. IN VACUUM TO 1000° C. AND QUENCHED IN MERCURY. × 100.

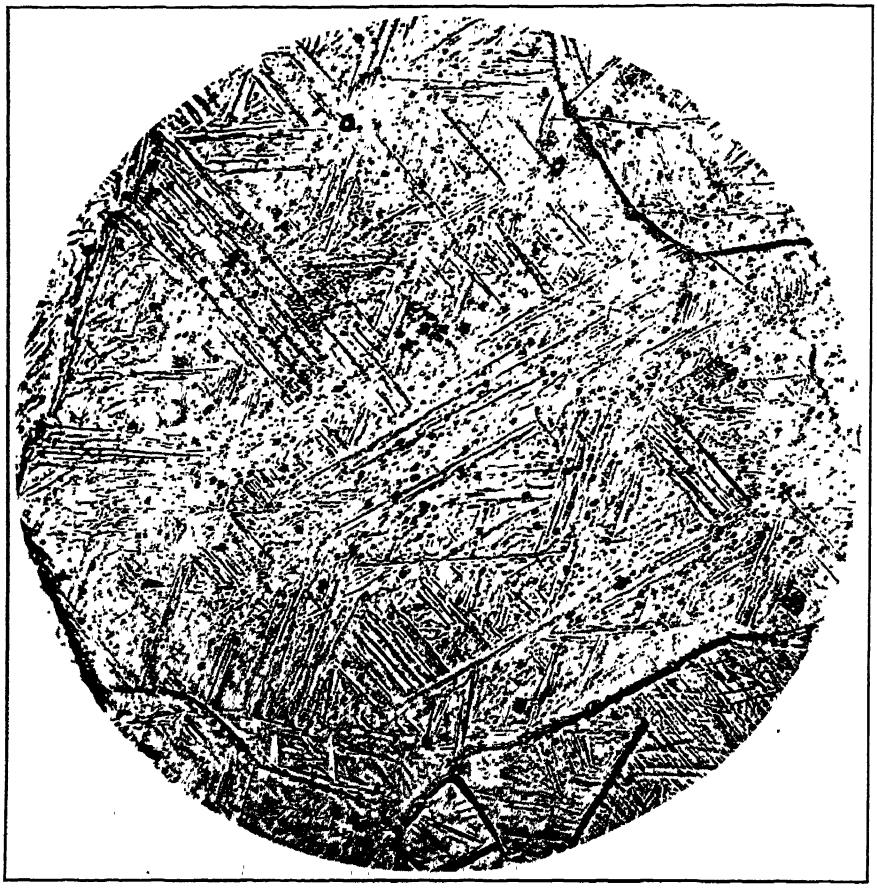


FIG. 5.—STRUCTURE OF POLISHED SURFACE OF ELECTROLYTIC IRON HEATED 2 HR. IN VACUUM TO 1000° C. AND QUENCHED IN MERCURY. × 500.
(Reduced to 3/5 original size; original magnification given.)

here clearly revealed. The alpha phase forms first along the crystallographic planes of the austenite and around the grain boundaries. Owing to the increased volume involved in the transformation, the new constituent stands in relief, as shown under high magnification. In Fig. 7 the image was focussed on the valleys, causing them to appear light, while the constituent standing in relief, including the boundaries, are dark. In Fig. 8 the image was focussed on the ridges causing the reversed appearance, the relief constituent being bright and the valleys dark.

It is natural to suppose that the martensitic pattern which has just been described is merely a surface phenomenon resulting from the fact that the alpha phase at the instant of its formation stood in relief in respect to the groundmass surrounding it. After polishing on No. 000 emery paper and alundum, all pattern was obliterated (Fig. 9). The black spot is a depression resulting from a Rockwell hardness test. The

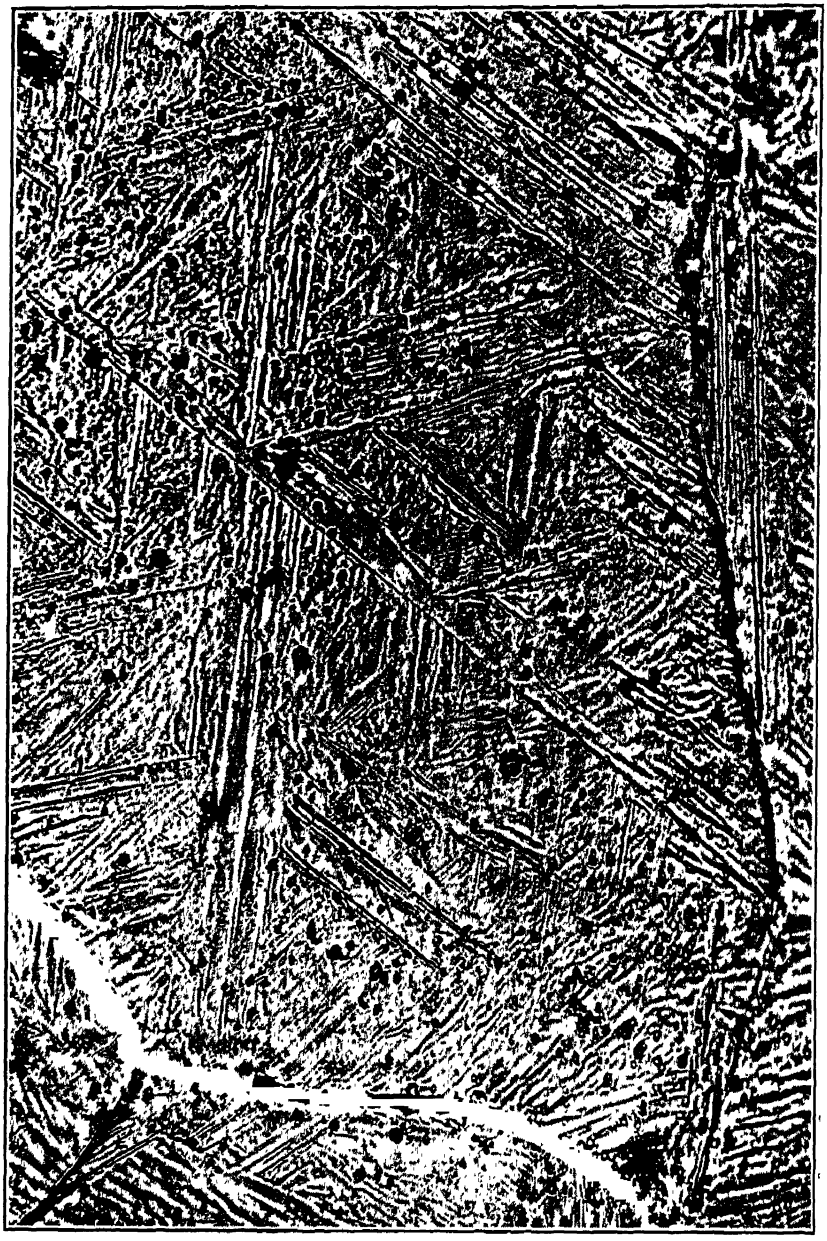


FIG. 6.—STRUCTURE OF POLISHED SURFACE OF ELECTROLYTIC IRON HEATED 2 HR. IN VACUUM TO 1000° C. AND QUENCHED IN MERCURY. × 800.
(Reduced to 4/5 original size; original magnification given.)

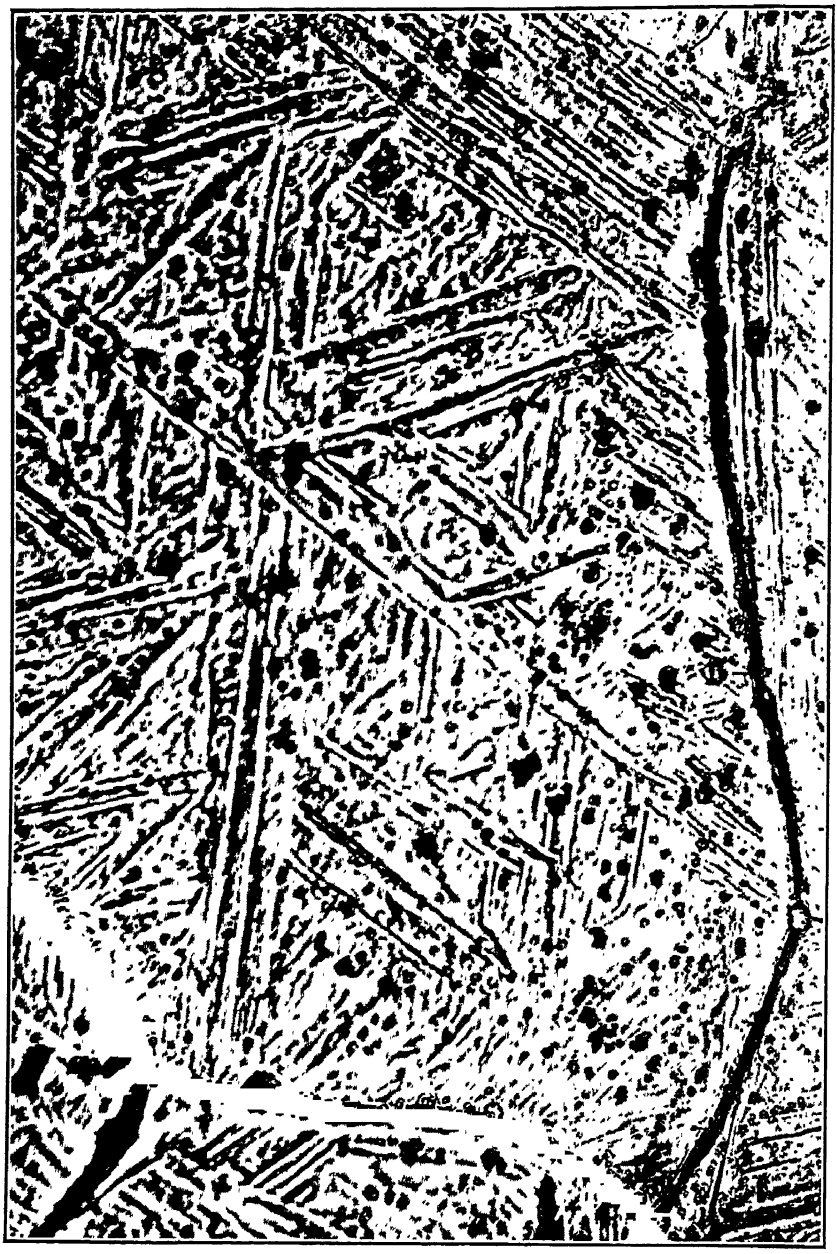


FIG. 7.—STRUCTURE OF SAME SPOT AS SHOWN IN FIG. 6, BUT FOCUSSED ON CONSTITUENT STANDING IN RELIEF. × 800.
(Reduced to 4/5 original size; original magnification given.)

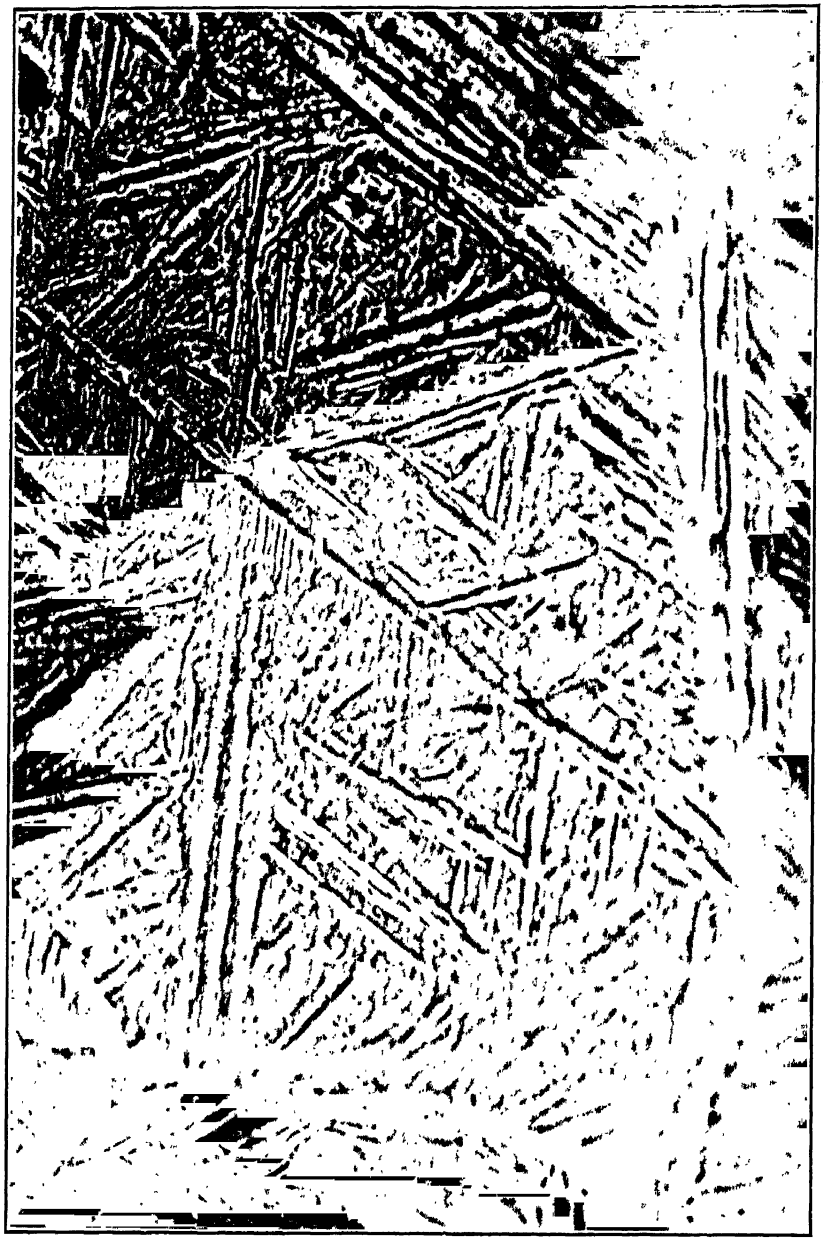


FIG. 8.—STRUCTURE OF SAME SPOT AS SHOWN IN FIGS. 6 AND 7, BUT FOCUSSED ON CONSTITUENT FORMING VALLEYS. × 800.
(Reduced to 4/5 original size; original magnification given.)

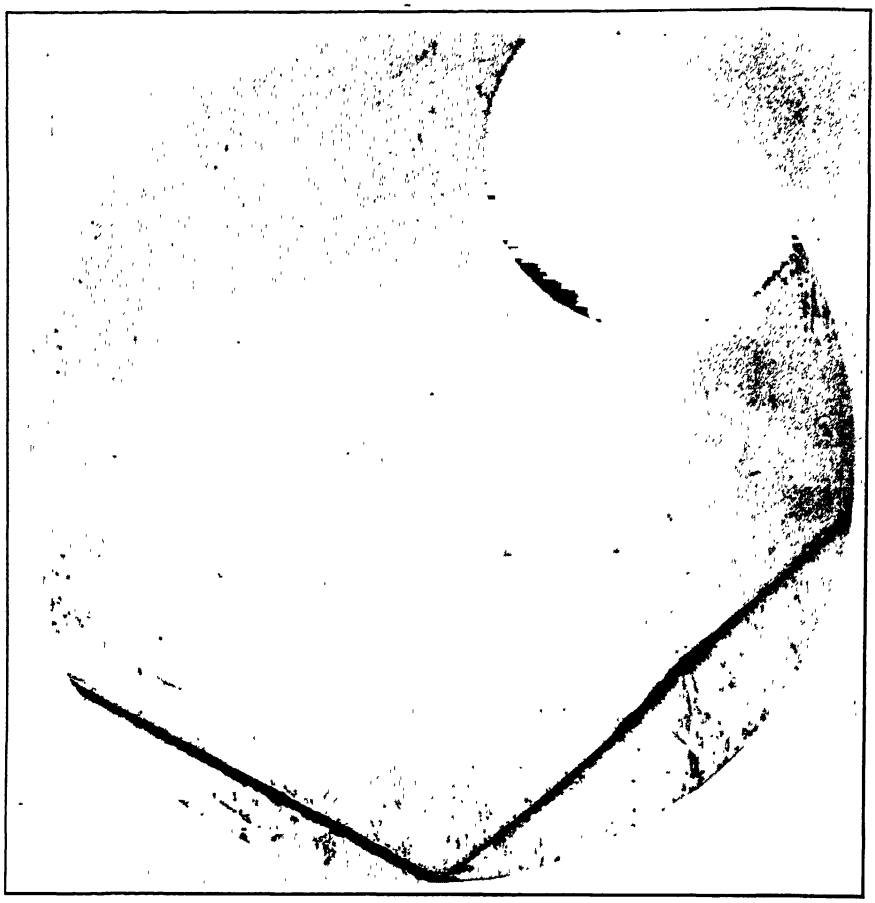


FIG. 9.—STRUCTURE OF POLISHED SURFACE OF ELECTROLYTIC IRON HEATED 2 HR. IN VACUUM TO 1000° C. AND QUENCHED IN MERCURY; AFTER SLIGHT REPOLISHING. × 50. (Reduced to 4/5 original size; original magnification given.)

black lines are identification marks. On etching the same repolished sample, a martensitic structure reappears, except in a few grains (Fig. 10). After polishing, starting with No. 0 emery paper, and etching, the martensitic structure was again revealed (Fig. 11), and likewise after starting polishing with No. 1 paper and etching (Fig. 12). That the martensitic structure resulting from the drastic quenching outlined above penetrates to a substantial depth is therefore apparent.

Under higher magnifications the types of structure generally associated with the so-called Widmanstättian patterns are clearly seen (Figs. 13 and 14). Indeed there seems to be little doubt but that the martensitic and the Widmanstättian types of structure are closely related. They both result from the deposition of the alpha phase along the crystallographic planes of austenite. The Widmanstättian structure

FIG. 10.—SAME SPOT AS SHOWN IN FIG. 9 AFTER ETCHING WITH 5 PER CENT NITAL. × 50.
(Reduced to 4/5 original size; original magnification given.)

in iron-carbon alloys results from slow cooling through the transformation points, the alpha phase being finally converted into free alpha ferrite (in hypoeutectoid steel), while the gamma phase after it has acquired eutectoid composition is converted into pearlite. The martensitic type of structure results from a rate of cooling so rapid that the transformations are delayed until a temperature of some 300° C. is reached. Under these conditions, the transformations remain incomplete, the alpha phase possibly retaining some carbon in solution while rejecting carbon in the form of minute particles of cementite and being thereby, in our opinion, converted into troostite. Some gamma phase holding considerable carbon in solution remains undecomposed when it is known as "retained austenite." The aggregate of these two phases constitutes, in our opinion, what is generally described as martensite. That the martensitic

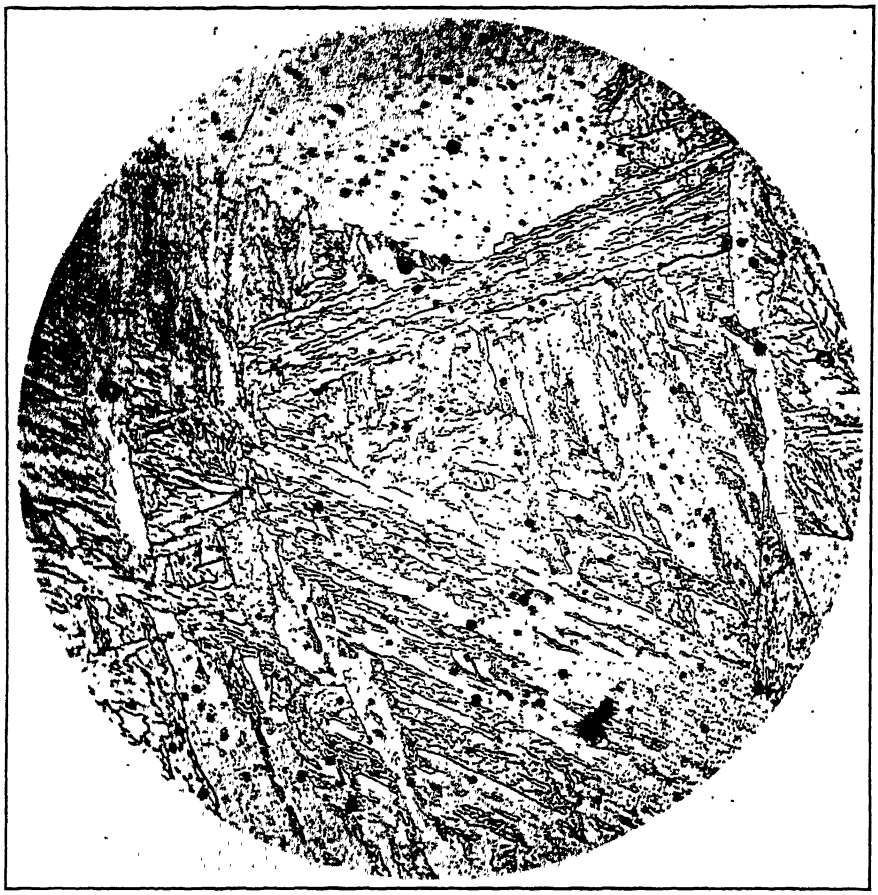


FIG. 13.—STRUCTURE OF POLISHED SURFACE OF ELECTROLYTIC IRON HEATED 2 HR. IN VACUUM TO 1000° C. AND QUENCHED IN MERCURY, AFTER SLIGHT REPOLISHING AND ETCHING IN 5 PER CENT. NITAL. × 500.
(Reduced to ¾ original size; original magnification given.)

surface of the grains by the transformation that took place at high temperature, like the imprints of boundaries of austenitic grains on the polished surface of steel samples heated within the austenitic range in vacuum. The authors do not call these constituents alpha and gamma iron, neither do they describe any physical characteristics by which the constituents can be distinguished one from the other, except that one stands out in relief and the other is found in depression. If the whole difference between the two is only in their level, it is rather difficult to prove the existence of two separate phases in the martensitic pattern. Perhaps the parallel ridges and valleys may be interpreted as the marks of mechanical disturbance produced in the crystalline pattern of grains by severe straining of the metal in unusually rapid cooling. This disturbance should naturally have followed the boundaries and the crystallographic planes of the grains, as the easiest ways, and might have created ridges and valleys in the same manner as slip bands or Neumann lines are created by the application of an external force. We know that pressure can develop grain boundaries and the cleavage planes in pure lead. In all these phenomena no physical changes are

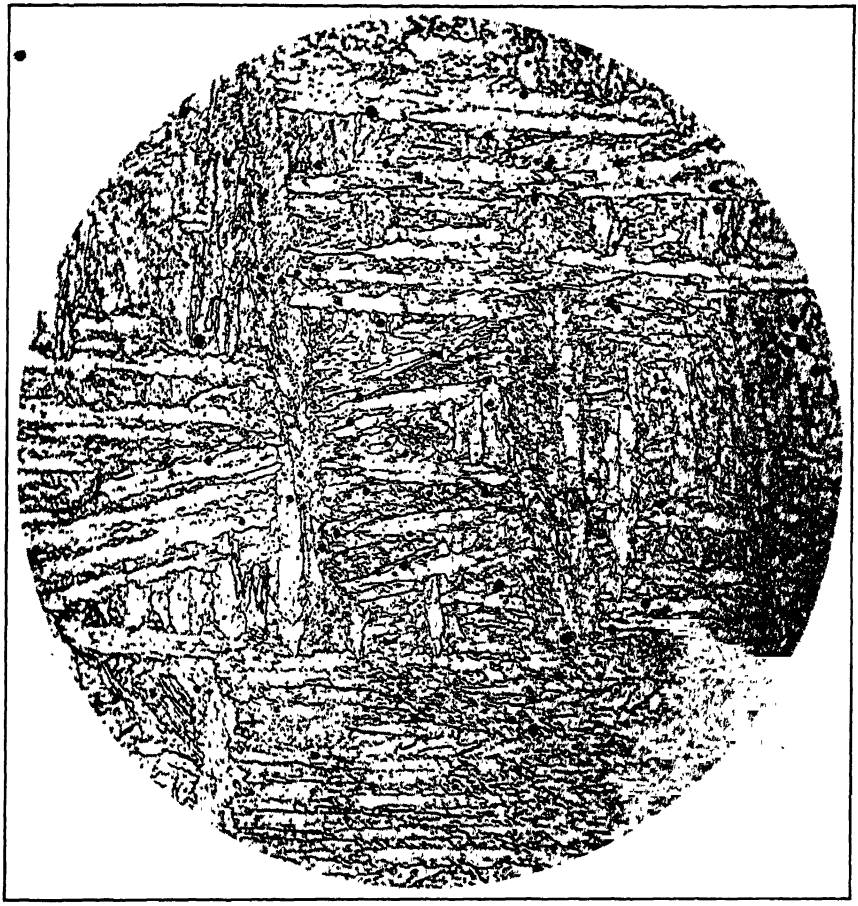


FIG. 14.—SAME SAMPLE AS SHOWN IN FIG. 13; ANOTHER SPOT. × 500.
(Reduced to ¾ original size; original magnification given.)

suspected and they should be interpreted as certain disturbances in the crystalline pattern effecting the bond between the adjacent grains and between certain crystalline units within the grains along their crystallographic planes.

Martensitic pattern is, of course, only one of many characteristic features of martensite itself and cannot be offered as a descisive proof of the existence of martensite This pattern is found in nonferrous alloys, such as bronze and brass, and in other metals.

The authors were entirely right in pointing out a close similarity between martensitic pattern and Widmanstättian structure. We know that ferrite in some highly overheated steels appears divided in parallel blocks and exhibits typical Widmanstättian structure. In the authors' samples examined under high power, see Figs. 13 and 14, the martensitic pattern was practically resolved into Widmanstättian structure in ferrite. From our viewpoint both patterns are closely related and should be interpreted as the structures in which crystallinity of grain was made more evident than in ordinary polygonal structure. As in all other crystalline bodies, crystall-

inity of ferrite may remain hidden or may be brought out to evidence by some factors, like overheating, straining or quenching, without necessarily involving a phasial change.

In the first series of experiments, the martensitic pattern in electrolytic iron was found purely superficial; in the second series, when mercury was used as quenching medium, it was found penetrating to a considerable depth. Beside all other considerations referred to, the effect of mercury on iron must also be considered. Though mercury does not amalgamate iron by direct contract, yet they form a compound FeHg and the superficial penetration of mercury in iron at high temperature may be suspected.

C. BENEDICKS, Stockholm, Sweden (written discussion).—It is always of considerable interest to see a consequence of the allotropy theory verified, even if there was not much reason to doubt this consequence. Though well known since Osmond that, in the presence of carbon, wedgelike alpha crystals, or martensite "needles," are formed in the gamma solid solution, or austenite, as groundmass, when this is cooled suddenly, and that they are crystallographically orientated according to the gamma-lattice, nobody had proved, before the present paper, that the same mechanism occurs in the absence of carbon.

One point, however, is perhaps not emphasized there clearly enough. As a matter of fact, a reader might obtain the impression that the mode of transformation illustrated in the paper must occur likewise on slow cooling through the point A_3. It will actually be necessary to make a clear distinction between (1) slow cooling and (2) rapid cooling through A_3, in the case of a pure iron.

1. On a very slow cooling, gamma as well as alpha iron are stable at the temperature A_3. Hence a loss in heat will have but a weak influence: that of causing those portions of alpha iron to be transformed into gamma iron *which are most easily transformed.* This necessarily is the case with the alpha iron situated in the grain boundaries, and quite especially at the corners, as here the atoms naturally possess a higher degree of freedom than inside the atomic lattice (or represent a less stable condition). In consequence, as well known, the alpha grains formed at A_3 show new boundaries, centering around the corners of the former gamma grains.

2. On a rapid cooling this tendency of transformation at the boundaries must be expected likewise to be the first one to accur. The rather striking fact that in the micrograms given no alpha particles in relief are to be observed at the boundaries is, however, easily explained by the long heating (2 hr.) at 1000° *in vacuo*, during which the metal near the boundaries has been volatilized (so that deep furrows are formed), a fact—rightly mentioned by the authors (p. 351)—which is precisely due to the same cause; *viz.*, the lower stability of the metal in the boundaries.

However, on account of the rapid cooling, the gamma metal will be undercooled, thus obtaining at any point the tendency of transforming into the stable alpha form, and this transformation having started at a given point in the gamma iron will proceed most easily along certain (octahedral) planes of the gamma iron (probably in first line on account of the volume change involved), as illustrated so well in the paper.

3. There will naturally be a medium cooling rate, at which the transformation to a great extent proceeds from the corners but at which, in the larger grains, the crystallographically orientated transformation will occur.

Generally, however, at ordinary cooling, the transformation will occur according to method 1, at least there is then no reason why the transformation should start inside the grains.

It might be added that the separation of alpha iron follows the same law as the separation of cementite from an austenite which has been saturated at a high temperature. On slow cooling, cementite is exclusively precipitated at the corners and in the boundaries in general. When the cooling is quicker, cementite is known to be

precipitated also in the interior of larger grains, forming thereby crystallographically orientated lamellae.[3]

P. DEJEAN, Grenoble, France (written discussion*).—The most striking point in the important work of Messrs. Sauveur and Chou is the conclusion they reach regarding martensite, when they say that this constituent is an aggregate of two phases. The writer expressed the same idea in his discussion of the paper by Mr. Sauveur in 1926.[4] The following is quoted from that discussion:

"All the tests performed with martensite, such as determination of the discontinuity of ferromagnetism, dilatation at 210°, X-ray examinations, etc., agree in showing that in that constituent iron is to a great extent in the alpha condition and that there is no free carbide present. On the other hand, seeing that the decomposition of martensite by gradual heating never yields graphite, but solely cementite and ferrite, it is logical to infer that martensite is a solid solution of carbide in alpha iron.

"There is one point, however, which should receive our attention, namely that from a microscopical point of view, martensite does not give the impression of a homogeneous constituent. Under very high magnification, one distinguishes clearly a needle-like constituent on a clear background. There seems to be two phases. As to their nature, several hypotheses may be offered. One might wonder if they are not two 'solutions' of the carbide Fe_3C, one in gamma iron (austenite) and the other in alpha iron. It is not impossible however, that in both solutions the carbide should be dissolved in alpha iron and that the only difference would consist in the percentage of carbide dissolved—in the same way that the solutions camacite and teamite of meteoric irons differ only by the proportion of nickel dissolved in the iron."

But, although the writer may agree with the authors on the subject of the existence of two phases in martensite, he does not agree with them in saying that, in martensite, the alpha phase "rejecting carbon in the form of minute particles of cementite and being thereby, in our opinion, converted into troostite." In fact, as he has indicated, no test has made possible the detection of the presence of free cementite in martensite, even in extremely fine particles.

E. C. BAIN, Kearny, N. J. (written discussion).—It is a most interesting contribution which Professor Sauveur and Dr. Chou offer in their paper, wherein electrolytic iron heated in vacuum and quenched shows the characteristic martensitic structure—even at some depth from the surface. There are several important deductions which they make aside from the direct evidence that the transformation in such nearly pure iron occurs by the same general mechansim as produces hard martensite in higher carbon steel. Their work decisively corroborates the view that the same crystallographic behavior of austenite is responsible for the appearance of the martensitic markings and also the familiar Widmanstättian structure. It becomes more than ever apparent that the octahedral planes of austenite are the only ones upon which alpha iron or carbide tend to form.

Now, as to the orientation of the alpha iron (in the one case as martensite with more or less carbon precipitated and in the other case as more or less laminated with carbide to form pearlite) we are still in doubt. It would be very interesting to have the views of Professor Sauveur and Dr. Chou on this point, particularly since in the quotation

* Translated from the French.

[3] See, for instance, C. Benedicks: Über das Gleichgewicht und die Erstarrungsstrukturen des Systems Eisen-Kohlenstoff. *Metallurgie* (1906) **3**, 393, 425, Fig. 14, or A. Sauveur: The Metallography and Heat Treatment of Iron and Steel, Ed. 2, 129, Fig. 150. Cambridge, Mass., 1916.

[4] A. Sauveur: The Current Theories of the Hardening of Steel Thirty Years Later. *Trans.* A. I. M. E. (1926) **73**, 890.

on the first page of the paper we read "There are good reasons for believing that it begins at the grain boundaries and along the octahedral planes of the crystals and that it progresses until each grain of gamma iron is changed into a grain of alpha iron, the resulting structure being similar to that of gamma iron," This sentence demands for its accuracy that all the various bits of alpha iron forming in cleavages and grain boundaries from one grain of austenite must possess the same orientation if they are to produce a single grain of alpha iron when they finally meet one another or that they rearrange later to accomplish this.

It would seem that another mechanism would also be possible depending upon the rate of cooling. To consider first an analogy, with one rate of cooling a melt of a pure metal or solid solution we develop columnar grains as a result of the fact that each liquid atom upon attaching itself to the previously solid material accepts the orientation of the already solidified metal. If, however, the cooling rate is slow, a few nuclei may form "ahead" of the advancing columnar grains and set up a new and different orientation. Thus in the interior of an ingot we may find random equiaxed grains and only on the outside are the columnar grains dominant. Similarly, it would appear that with very slow rates of cooling gamma iron many nuclei might form within the mass and grow by adding atoms of iron. This would account for the polyhedral grains of alpha iron resulting from the solid grains of gamma iron. It has frequently been observed that the two grain boundry systems are dissimilar. The structures which Professor Sauveur and Dr. Chou have obtained would then correspond to a more rapid cooling in which the transformation follows the advance of an isotherm more approximately and therefore the new crystal form would have a more strictly controlled orientation, referring ultimately to the orientation of the austenite grains.

We are certainly greatly indebted to these authors for providing such clear evidence of the acicular structure in iron containing what must have been extremely little impurity.

G. E. DOAN, Bethlehem, Pa. (written discussion).—The value of careful investigation upon a problem of limited scope, such as Professor Sauveur has chosen, is always appreciated, especially when the work has been done with a good degree of accuracy. The paper indicates strongly that the gamma form of iron may be partially retained at room temperature by quenching a specimen of electrolytic iron in mercury. The effect of the greater amounts of impurities found in commercial iron alloys is, of course, to aid the quenching action by slowing down the rate of formation of alpha nuclei or the rate of growth of the alpha crystallites, or both, and thus of permitting some unchanged gamma iron to remain. As Dr. Mehl has pointed out, an X-ray spectrogram of the specimen would be necessary in order to state definitely the presence of the gamma iron.

The resemblance of the martensitic type of structure so produced to the Widmanstättian structure of slowly cooled hypoeutectoid steel is not surprising, since both arise from the same reaction; namely, from the precipitation of a newly emerging phase (alpha iron) in the crystallographic planes of the preexistent phase (gamma iron) The alpha-beta brasses show a similar appearance. The alpha constituent precipitates in the crystallographic planes of the original beta solid solution.[5] Another example is the precipitation of needles of cementite in the crystallographic planes (and at the grain boundaries) of hypereutectoid steel. Still another example of the Widmanstättian type of structure is the alloy of 25 per cent. tin and 75 per cent. silver. It thus appears that the structural features both of martensite and of Widmanstättian steel are merely special examples of a perfectly general habit of certain alloys which undergo changes in the solid state. The new phase, which is in equilibrium with the

[5] W. Rosenhain: Introduction to Physical Metallurgy, 144, Fig. 56. New York, 1915. D. Van Nostrand Co.

preexistent phase, precipitates as crystal fibers in the crystallographic planes, and at the grain boundaries. The precipitation of alpha iron in the cleaveage planes and at the grain boundaries of a gamma solid solution is, therefore, merely an individual case of this entirely general process.

Finally, the writer wishes to express his entire agreement with Professor Sauveur's introductory statement: "that when gamma iron transforms into alpha iron on reaching the A_3 point, each gamma grain does not change bodily into one or more alpha grains, but that the alpha phase forms first at the boundaries and along the crystallographic planes of the austenite grains." Tammann, in his studies of crystallization and melting (states of aggregation) shows that the formation of a new phase in one already present always takes place initially in small areas (points) or nuclei, widely distributed throughout the existent phase, from which points the new phase spreads and grows. This process of crystallization is essentially the same regardless of whether the parent phase is crystalline or liquid. Thus in an under cooled liquid, the beginning of crystallization is the appearance of crystalline nuclei. These nuclei are scattered throughout the melt, if the temperature is uniform throughout the melt, or concentrated along the walls of the container and top of the melt, if the temperature is lower there, as is the case under usual casting conditions, on account of the greater undercooling of the metal at these points. These and later crops of nuclei of the new phase (which may be considered as elementary cells of the space lattice of the new phase), now grow by the orderly accretion of atoms from the melt until the melt is entirely crystallized. An exactly similar process occurs when alpha iron crystallizes from gamma iron. The nuclei of alpha grains form at *points* in the existent gamma grains, usually in the crystallographic planes of the gamma grains and at the grain boundaries, and spread from these points throughout the entire mass. It is conceivable that only one nucleus should form in each gamma grain or that the numerous nuclei should gradually coalesce into a single alpha grain having the same boundaries as the mother grain, but certainly, in view of the mechanics of the process, one would not as, Professor Sauveur intimates, consider this as the most likely result. This "point origin" of a new phase, just outlined, holds also for the precipitation of salts from a supersaturated water solution, for the crystallization of a metallic vapor chilled below the melting point, and in general for the appearance of any new phase in an already existing phase. It is even evident in the recrystallization of a cold-worked metal, the new crystallites forming at points in the grain boundaries and in the crystallographic planes of the deformed metal, although this latter case cannot be called strictly a phase change.

There are many other examples of the type of formation when a new crystalline variety emerges in an existent one. The particles of Fe_3C of nearly colloidal size, which Lucas has shown in martensite, are nuclei of Fe_3C in an advanced stage of growth. They are separated from each other and illustrate again the point origin of a new crystalline phase from an existent one. When these particles have further coagulated as in annealed hypereuctectoid steel, they appear as crystal fibers in the crystallographic planes of the now partly transformed austenite.

An example of the reversed process, the appearance of melt in a crystalline phase, is given in the paper by Schumacher and Nix.[6] Here the new phase appears again at scattered points throughout the crystals and at the grain boundaries.

We thus see once more that the much-studied system iron-carbon does not belong in a class by itself, but is subject to precisely the same laws of physical chemistry as other alloy systems.

---

[6] E. E. Schumacher and F. C. Nix: The Solidus Line in the Lead-antimony system. *Proc.* Inst. Met. Div., A. I. M. E. (1927) 201.

R. F. MEHL, Anacostia, D. C. (written discussion).—This interesting paper suggests a number of questions, but before putting them I should like to propose a possible explanation of the structures shown so clearly in the photomicrographs.

Since its discovery in 1808 by Widmanstätten, the structure named after him has attracted from time to time considerable attention. It is now generally conceded that the Widmanstättian structure originates in a precipitation along the octahedral (111) planes in the face-centered cubic lattice, as Professor Sauveur points out, but so far as I know there has been no attempt to explain this selection of the (111) plane in gamma iron by the newly found alpha iron.

The study of the mechanism of plastic deformation in metals has shown that the (111) plane in the face-centered cubic lattice is the plane of least resistance to slip. It is well recognized that alpha iron forms from gamma iron with an increase in volume, yet it is difficult to see how even a localized volume increase could, by slip bring the (111) planes into such uniform relief as we have them in the Widmanstättian structure.

I should like to suggest as a possible reason for the selection of the (111) plane that it is this plane in the face-centered cubic lattice which possesses the least interplanar cohesion. If this be true, it seems reasonable that the alpha phase should form along this plane, since it is here that an expansion in volume can take place with the least expenditure of work.

Evidence can be adduced in support of this view from the work of Rosbaud and Schmid[7] in the strengthening of single crystals of zinc by alloying with cadmium and tin. It had previously been shown that the basal plane of the hexagonal zinc, the (0001) plane, is the plane of easiest slip, and that the $(10\bar{1}0)$ plane, prismatic plane of the first type, is next in the order of ease of slip but requiring a very much greater shearing stress per 1 mm. of gliding surface to initiate slip than the (0001) plane. In addition to this, and much more valuable for our present purpose, is the fact that the tensile stress normal to the (0001) plane necessary to induce rupture without appreciable slip (the necessary condition in a rapid rate of loading at the temperature of −180° C.) is also much less for the (0001) plane than any other in lattice. This latter fact seems to point conclusively to a lower interplanar cohesion for the (0001) plane. In the paper cited it was shown that zinc will hold less than 0.1 per cent. tin in solid solution at room temperature, but that when the tin is slightly in excess of this amount the zinc-tin eutectic precipitates in striae parallel to the (0001) plane as shown by Figs. 13 and 14. Assuming that at a higher temperature the solubility of tin in zinc is sufficient to hold all of it in solid solution, the precipitation therefore takes place preferentially on the basal plane, the plane of least interplanar cohesion, and it seems reasonable that it seeks this plane preferentially because it could there establish its own volume with the expenditure of the least work.

In the present paper, Figs. 10 to 14 show that the Widmanstättian structure visible on the polished surface of the specimen quenched in mercury (Figs. 4 to 8) is not purely a surface effect but can be reproduced after polishing by suitable etching. This seems to indicate that the alloy is heterogeneous, that some gamma iron is present, at least in the outer layer of the quenched piece. Has this layer been examined by X-rays for the characteristic gamma iron diffraction? If the metal is actually heterogeneous it should, judging from its structure, possess a high hardness, and I should like to ask if hardness measurements are available.

The regular precipitation of alpha iron on the octahedral planes suggests that its orientation may bear a simple crystallographic relation to the (111) plane upon which it appears. In such a case each gamma iron grain would transform into a single

[7] P. Rosbaud and E. Schmid: Über Verfestigung von Einkristallen durch Legierung und Kaltrschung. *Ztsch. f. Phys.* (1925) **32**, 197.

grain of alpha iron. That is, there would be no granulation during the transformation. I am curious to know whether Professor Sauveur has any observations on the history of any one gamma iron grain as it transforms into alpha iron.

A. SAUVEUR and C. H. CHOU (written discussion).—Referring to Mr. Polushkin's remarks, it is not believed by us that undecomposed gamma iron is retained by our quenching treatment, but we do believe that it reveals the mechanism of the gamma-alpha transformation as evidenced by the production and retention of a martensitic pattern. Severe straining may well have occurred at some of the crystallographic planes but we are inclined to consider this as the step immediately preceding the formation of alpha iron along the same planes. Mr. Polushkin refers to the possibility of developing by pressure along grain boundaries and cleavage planes in pure lead. It is believed that if lead underwent an allotropic transformation it is along these same boundaries and cleavage planes that the new phase would form first. We are pleased that the writer shares our belief in the similarity between the Widmanstättian and martenitic structures and we agree with him that our experiments reveal the crystallinity of austenite. We do not think, however, that such crystallinity could be brought out by our quenching experiment if iron did not undergo an allotropic transformation. Whatever the action of mercury on iron may be, it is difficult to conceive that it could produce a martensitic pattern on the polished samples.

We are grateful to Dr. Benedicks for his clear and well supported view of the gamma-alpha transformation (1) on slow cooling and (2) on rapid cooling.

The positive statement of Dejean that the alpha constituent or constituents in martensite do not contain any particles of cementite and must therefore be considered as a solution or as solutions of carbon in alpha iron should receive careful consideration. We are inclined to believe that while at the instant of its formation—that is, in the quenching bath—the alpha phase may retain carbon in supersaturated solution, the latter is so unstable that precipitation of carbide in a finely divided condition soon follows.

The question whether in the gamma-alpha transformation each grain of gamma iron finally transforms into a grain of alpha iron is pertinently asked by Dr. Bain. We have no evidence to offer. The speed of cooling may well be a determining factor. The problem calls for further investigation.

We agree with Professor Doan in regard to the wide application of the phenomenon described in our paper: namely the location of a new phase along the crystallographic planes of the mother phase. In the case cited by him, however, the mother phase is a solid solution whereas we are dealing with the allotropic transformation of a pure metal. As already stated we do not believe that gamma iron is actually retained in our quenching experiment but that the pattern obtained reveals the mechanism of the transformation of gamma iron into alpha iron.

Dr. Mehl's suggestion that the alpha phase forms selectively along the parallel planes of the face-centered cubic lattice of the gamma iron because these planes possess the least interplanar cohesion and therefore offer better opportunity for expansion is very welcome and well supported by the behavior of single crystals of zinc alloyed with cadmium and tin, as described by him.

Some X-ray diffraction patterns were taken of the polished surfaces exhibiting martensitic structures, but no gamma lines could be detected. It is not believed that any gamma iron is actually retained after drastic quenching of electrolytic iron. Scratch hardness tests were made of some of the samples and it was found that the quenched specimens were appreciably but not greatly harder than the original electrolytic iron. We have not attempted to follow the transformation of any particular gamma grain.

Change in Microstructure of Iron at A_3 Transformation Point

By B. A. Rogers,* Chicago, Ill.

(Cleveland Meeting, September, 1929)

The etching effect that is produced on a piece of polished iron or steel when it is heated in hydrogen or in a vacuum seems to have been observed first by Osmond,[1] who believed that he could distinguish four systems of grain boundaries on a piece of steel which had been heated in hydrogen. In a number of other investigations, samples of pure iron were found, after heating, to have complex networks in which two or three systems of grain boundaries could be detected. It was further noticed that samples that had been polished plane before being placed in the furnace were, after treatment, roughened and undulating over their entire surfaces. From a comparison of the temperature of heat treatment with that of the A_3 transformation, it was concluded that the changed appearance of the samples was definitely related to the latter phenomenon. Certain other deductions were made but these are not of importance here and only observations on the appearance of the samples will be reviewed.

Ewen[2] heated a strip of polished iron in a vacuum in such a way that one end was maintained at a temperature of 1000° C. and the other at 580° C. On the cooler end there was outlined a simple polyhedral network, and at the hotter there appeared the complex system of lines and the undulating surface characteristic of iron which has passed through the A_3 transformation. He found that in going from the cooler toward the hotter end the sample maintained much the same character of surface up to the beginning of the transformed area, but that near this region double grain boundaries were of frequent occurrence. Rawdon and Scott[3] concluded that the simple type of network brought out by heating a sample of pure iron in a vacuum was of the same type as that developed by ordinary etching methods. They also confirmed the observations of

* Western Electric Co.

[1] F. Osmond: Sur la Cristallographie du Fer. *Ann. des Mines* [9] (1900) **17**, 110. F. Osmond and G. Cartaud: Sur la Cristallographie du Fer. *Ibid.* (1900) **18**, 113.

[2] D. Ewen: The Structural Changes of Iron during Annealing. *Intl. Ztsch. f. Metallog.* (1914) **6**, 1.

[3] H. S. Rawdon and H. Scott: Microstructure of Iron and Mild Steel at High Temperatures. U. S. Bur. Stds. *Sci. Paper* 356 (1920).

Rosenhain and Humfrey[4] that there was no particular structure which could be connected to the range between the A_2 and A_3 transformation points. They did find a kind of branching effect which appeared to be like that sometimes seen on pure iron etched by ordinary means; that is, rather faint grain boundaries within the more prominent network, when the iron was taken up well toward 900° C.

These investigators and others[5] have described the appearance of samples subjected to heat treatment at various temperatures rather completely but the attempt to watch the change in microstructure as the iron goes from the alpha to the gamma state seems not to have been made. The writer has seen this phenomenon take place and has found it interesting to observe.

Apparatus Used in Experiments Described Herein

The furnace used in this work differs somewhat from any of those described in the literature for heating samples that were being observed microscopically, of which two are notable. The first has for a heating element, a strip of platinum on which can be placed small samples of metal, the melting point of which is to be observed. It is a part of the apparatus known as the Burgess micropyrometer.[6] The other, described by G. Friedel,[7] is of the type used in mineralogical work. Its upper limit with respect to temperature is considered to be 400° C.

Fig. 1 shows a sketch of the furnace used in this investigation. The furnace has three principal parts: the water-cooled brass outer shell, the water-cooled brass lid with its transparent fused silica window, and the central arrangement for heating the sample. The last consists of the tungsten wire I wound on alundum cylinder E, specimen support F, thermocouple G, metal shields K and the short silica cylinder H. Alundum cylinder E is held firmly in position by the granular magnesia which fills the space between it and the outer shell.

The inside diameter of the outer shell is about 73 mm. and the height from the floor to the cover is about 63 mm. The inside diameter of alundum cylinder E is approximately 13 mm. The wire with which it is

[4] W. Rosenhain and J. C. W. Humfrey: The Crystalline Structure of Iron at High Temperatures. *Coll. Researches*, Natl. Phys. Lab., Teddington (1910) **6**, 189.

[5] A. Kroll: The Crystallography of the Iron-Carbon System. *Jnl.* Iron and Steel Inst. (1910) **81**, 314.

J. C. W. Humfrey: The Intercrystalline Fracture of Iron and Steel. *Carnegie Schol. Mem.* Iron and Steel Inst. (1912) **4**, 80.

[6] G. K. Burgess: A Micropyrometer. *Bull.* U. S. Bur. Stds. (1913) **9**, 475

G. K. Burgess and R. G. Waltenberg: Melting Points of the Refractory Elements —I. Elements of Atomic Weight from 48 to 59. *Bull.* U. S. Bur. Stds. (1914) **10**, 79.

G. K. Burgess and R. G. Waltenburg: Emissivity of Metals and Oxides.—II. Measurements with the Micropyrometer. *Bull.* U. S. Bur. Stds. (1914–15) **11**, 591.

[7] G. Friedel: Modele de four electrique pour le microscope. *Rev. d'Optique* (1927) **6**, 34.

wound has a diameter of 1 mm. The alumel and chromel thermocouple wires are 22 gage. The total thickness of the cover is about 6 mm. The window at its center is a circular plate about 1 mm. thick and 9 mm. dia. The vertical position of the specimen support is governed by the working distance of the objective. The 24-mm. objective used in these experiments had about the same working distance and the height of the speci-

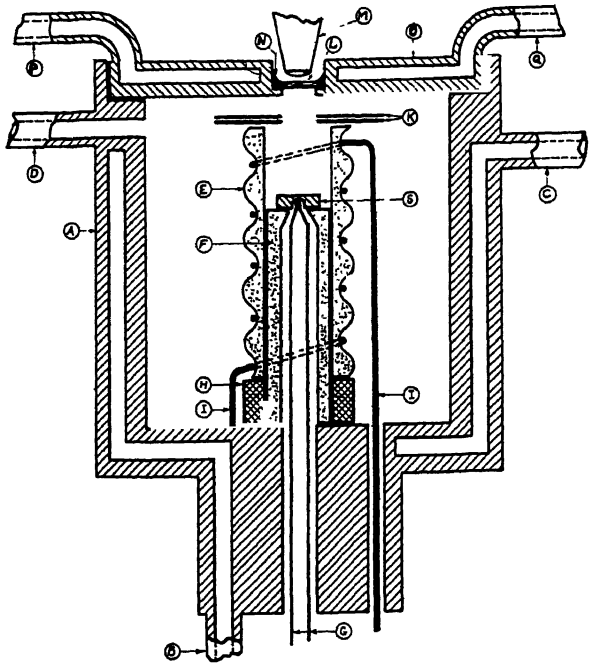


FIG. 1.—SKETCH OF FURNACE.

A. Furnace outer shell
B. Water inlet
C. Water outlet
D. Hydrogen inlet
E. Threaded alundum cylinder
F. Alundum specimen support
G. Thermocouple
H. Silica support
I. Heating element
K. Metal shielding disks
L. Fused quartz plate
M. Microscope objective
N. De Khotinsky cement
O. Furnace cover
P. Water outlet from cover
Q. Water inlet to cover
S. Specimen

men support was therefore arranged to bring the upper surface of the specimen about 18 to 20 mm. below the lower surface of the window.

Besides the furnace there was required a Leeds and Northrup potentiometer indicator of the portable type, a small transformer, tapped to give up to 16 volts by 1-volt increments, for supplying the heating current, a tank of compressed hydrogen, and a microscope with an illuminator of the type used in visual metallographic work. The upper part of the microscope was removed from its base and mounted on a vertical cylinder which could be rotated about its axis. When so mounted, it could be

easily swung to one side when changing specimens. The power supplied by the transformer at 16 volts was sufficient to bring the temperature of the furnace to 1100° C. Just how high it would be possible to heat the furnace without melting the DeKhotinsky cement, which holds the window in place, or ruining an objective cannot be stated, but the limit appeared to be considerably above 1100° C.

Wave Change in Microstructure

The change in microstructure could be easily and clearly seen through the silica window. It took place as an eruptive wave which passed with surprising speed over the surface of the sample and left it completely changed in appearance. That the wave had its origin in the rearrangement of space lattice, which takes place not far above 900° C., was determined by finding, with some degree of accuracy, by the method to be described in the next paragraph, the temperature at which it passed. Samples used for this work were cut from a forged piece of vacuum-melted electrolytic iron. This material was not analyzed, but a ring of the same material had a permeability above 21,000 when annealed in a vacuum for one hour at 895° C. In shaping up the samples, the surface was ground off to a depth of 1 mm., to eliminate any impurities picked up in the forging process. The samples were then drilled nearly through, as shown in Fig. 1, in order to fit down over the junction of the thermocouple.

In determining the temperature at which the change in microstructure occurred, it was soon found unnecessary to keep the potentiometer balanced all the time, as it was much easier to set the dial at the approximate reading at which the transformation occurred and then to watch the slow progress of the galvanometer needle across the scale. By experiment it was found that a deflection of one division off zero of the galvanometer needle corresponded to a correction of 0.015 mv. to the dial setting. By this method the transformation could be detected by the stopping or arrest of the galvanometer needle as the absorption or evolution of heat incident to the transformation caused the temperature to remain constant for a short time. It was ordinarily possible to set the dial so that the arrest and the wave occurred when the needle was within one division of the zero mark. Two observers were required, one to watch the sample and the other to read the potentiometer.

The melting points of two samples of pure silver were used as a one-point calibration of the thermocouple. The samples were of about the same dimensions as the specimens of iron and their melting point was determined by observation and by the arrest of the galvanometer needle. Fortunately, it was possible to avoid complete melting by shutting off the power so that the thermocouple remained intact. Using 960.5° C. as the melting point of silver, it was determined that the readings were about

1.6 per cent. too low and values for the iron samples were raised a corresponding amount. A typical run on one of these samples is shown in Table 1.

TABLE 1.—*Typical Run on Sample*

Power on at 10:15 Room Temperature, 23° C.
Transformation temp. reached at 10:30 Potentiometer Cor., 1.57 mv.

Direction of Temp. Change	Arrest, Millivolts	Wave, Millivolts	Arrest, Deg. Cent.	Wave, Deg. Cent.	Volts on Trans.
Rising.....		37.85		911	13
Falling.....	37.4	37.4	900	900	11
Rising.....	37.95	37.95	913	913	14
Falling.....	37.3	37.3	897	897	9
Rising.....	37.8	37.8	909	909	16
Falling.....	37.4	37.4	900	900	12
Rising.....	37.9	37.95	912	912	13

Power off at 10:43.

The waves after the first usually caused much less change in the surface than the original eruption, although in a few cases the wave on rising for the second time appeared to alter the appearance of the sample almost, if not quite, as much as the first. For the most part the later waves had an appearance like that of water running rapidly over a dry surface. They might also be likened to a shadow passing along.

TABLE 2.—*Averages of Ten Samples*

Sample	Temperature Rising		Temperature Falling	
	Arrest, Deg. Cent.	Wave, Deg. Cent.	Arrest, Deg. Cent.	Wave, Deg. Cent.
1	911	911	897	897
2	913	914	898	898
3	913	914	898	898
4	909	908	897	897
5	910	912	900	900
6	911	911	899	899
7	911	913	899	899
8	909	909	899	899
9	909	910	900	900
10	914	915	900	900
Average.....	911	912	899	899

FIG. 2.—VACUUM-MELTED ELECTROLYTIC IRON HEATED JUST BELOW 900° C. × 51.
FIG. 3.—SAMPLE OF FIG. 2 WITH A_3 TRANSFORMATION JUST BEGINNING. × 51.
FIG. 4.—SAMPLE OF FIG. 2 WITH TRANSFORMATION FURTHER ADVANCED. × 51.
(Reduced 25 per cent., original magnification given.)

The temperature at which the waves passed did not show any consistent dependence on the rate of heating or cooling. The slowest rate of rise was about 10° C. per minute or a little less, obtained by using the 13-volt tap, while with 16 volts across the furnace winding, the rate of rise was in excess of 100° C. per minute.

A series of 10 samples was tested in the same manner as the one just discussed and the average temperature of both wave and arrest was computed. The averages for the 10 samples were then obtained and gave 911° C. for the average arrest with rising temperature and 912° C. for the average temperature of the passage of the wave. With the sample cooling, the average values for both arrest and wave were 899° C. The averages for the 10 samples are shown in Table 2.

From an inspection of these results there seems little reason to doubt that the change of microstructure occurs simultaneously with the A_3 transformation.

It would no doubt be a simple matter to photograph the sample while it is in the furnace but the method seemed to offer little advantage over that of removing it and taking a picture in the ordinary way, as it is easy to stop the transformation at any stage. Figs. 2 to 6 show photomicrographs of sample No. 8, repolished after an anneal in hydrogen at 1100° C. for 24 hr.[8] passing through the transformation by stages. In Fig. 2 is shown the simple structure which develops by heating below 900° C. Fig. 3 shows the beginning of the transformation. The wave had come in from the left as far as the irregular line and was also coming down from the top. The widening of the grain boundaries just preceding the passage of the wave is one of the phenomena characteristic of the transformation. A double grain boundary, which is probably of the variety mentioned by Ewen, is to be seen in the upper right part of the photograph. A part of this double boundary is faintly visible in the original of Fig. 2. In Fig. 4 all the surface, except that at the right, has been transformed. Fig. 5 shows the sample completely transformed and much broken up. As the sample was heated and cooled through the transformation range, its surface continued to display additional lines and after five cycles appeared as in Fig. 6. All photographs in this series were taken at a magnification of 51 diameters.

Figs. 7 and 8 show the eruptive wave in progress on material from the same forged piece but not annealed as described for the sample of the foregoing series. The difference in structure between these two may be due to an annealing of one of them by previous runs in the furnace. It will be remembered that all transformed areas shown in the photograph have actually passed through the A_3 point an even number of times.

Samples of Armco iron which had been annealed in commercial nitrogen for 24 hr. at 1150° C. showed an interesting change in microstructure.

[8] The temperature once rose to nearly 1250° C. during this run.

Beginning 20° to 30° C. or even more, below the usual temperature of phase change, pits would form at the junctions of the grain network and gradually increase in area up to the transformation of the body of the metal. This action suggests an intergranular penetration of the nitrogen with consequent lowering of the A_3 point in the parts of the grain adjacent to the boundary. A photograph of such a sample is shown in Fig. 9.

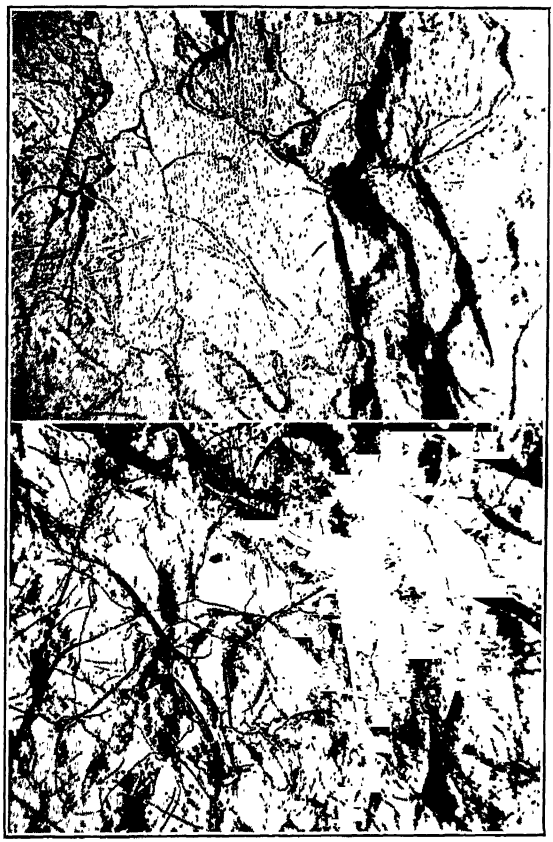


FIG. 5.—SAMPLE OF FIG. 2 WITH TRANSFORMATION COMPLETED. × 51.
FIG. 6.—APPEARANCE OF SAMPLE AFTER PASSING THROUGH TRANSFORMATION SEVERAL TIMES. × 51.
(Reduced 25 per cent., original magnification given.)

The action of the sample annealed in nitrogen suggests that the presence of any considerable amount of an element that forms a eutectoid with iron might eliminate the eruptive wave altogether, since the transformation then takes place over a range rather than at a definite temperature. In agreement with this hypothesis is the fact that samples of structural steel displayed no wave although their appearance at high temperature was considerably different from that at low temperature. On the other hand, the existence of a temperature range for the change

FIG. 7.—VACUUM-MELTED ELECTROLYTIC IRON WITH A_3 TRANSFORMATION IN PROGRESS. × 100.

FIG. 8.—ANOTHER SAMPLE OF VACUUM-MELTED ELECTROLYTIC IRON UNDERGOING TRANSFORMATION. × 100.

(Reduced 25 per cent., original magnification given.)

of phase is not necessarily inimical to a sudden change of microstructure, for an iron-cobalt alloy containing 55 per cent. of cobalt displayed a very distinct disruptive wave at the temperature of the shift of space lattice.

Since the change in microstructure in pure iron occurs at the transition of space lattice, the question arises as to whether cobalt will exhibit a similar phenomenon when its space lattice changes.[9] With this question

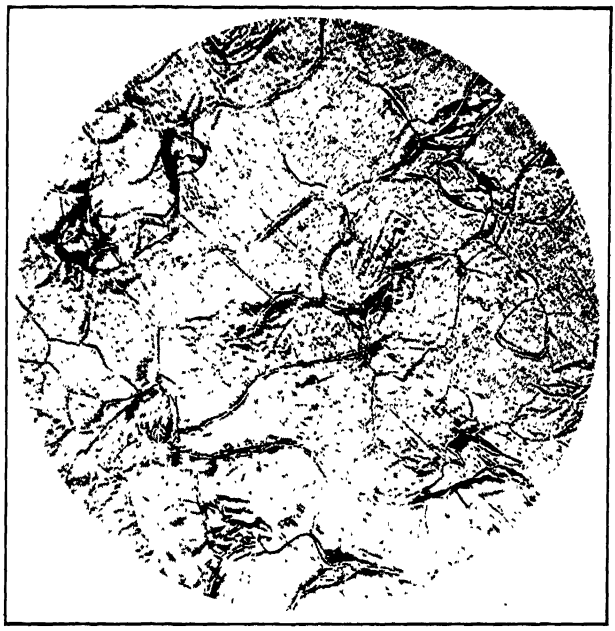


FIG. 9.—PITTED APPEARANCE OF ARMCO IRON, ANNEALED IN NITROGEN, AS TRANSFORMATION IS BEGINNING. × 100.
(Reduced 25 per cent., original magnification given.)

in mind a piece of polished cast cobalt of unusual purity was placed in the furnace and heated slowly. A few markings appeared as early as 400° C. but no change of any magnitude occurred until there developed at 445° or 450° C. a set of geometric figures, triangles, approximately equilateral, parallelograms and trapezoids which appeared to stand out in relief. The appearance of these figures was not nearly so sudden as was the wave on pure iron, a fact perhaps partly to be accounted for by the greater rigidity of the metal at the lower temperature, and partly by the presence of small amounts of impurities. Unfortunately for the purposes of photography, the geometric figures lost their distinctness as the sample cooled.

[9] H. Masumoto: New Transformation of Cobalt and the Equilibrium Diagrams of Nickel-Cobalt and Iron-Cobalt. *Sci. Repts.* Tohoku Imp. Univ. [1] (1926) **15**, 449.
W. C. Ellis: Study of the Physical Properties of Electrolytic Cobalt and Its Alloys with Iron. Rensselaer Poly. Inst. Eng. and Sci. Ser. No. 16 (1927).

The work done in this investigation confirms the results of previous investigators in that there is no appreciable change in the microstructure of iron until the A_3 point is reached. It further appears, if the iron is pure, that the change comes simultaneously with the changes in heat content and space lattice. The results obtained also agree with theoretical considerations in that the presence of an element which forms a eutectoid with iron reduces the distinctness of the eruptive wave or causes it to disappear altogether. The action of iron and cobalt, and to a lesser extent of their alloy, indicates that a sudden change in microstructure is connected with a fairly abrupt shift in space lattice.

Acknowledgments

The author has pleasure in acknowledging his indebtedness to his wife and to his colleagues at the Western Electric Co., particularly J. L. Gregg, H. S. Van Vleet, A. L. Dixon, and A. L. Kirby, for helpful suggestions and other assistance during the course of the work.

DISCUSSION

N. A. Ziegler, East Pittsburgh, Pa. (written discussion).—Mr. Rogers must be congratulated for a valuable and excellent piece of research. In 1924 the writer performed several crude experiments, similar in principle to those described by Mr. Rogers. The object was to observe visually the transformations that take place in iron and its alloys, when heated to high temperatures.

The furnace used resembles closely the one described by Mr. Rogers, the points of distinction being: (1) Vacuum was used instead of hydrogen atmosphere; (2) the heating element was a nichrome ribbon instead of tungsten wire; and (3) it was mounted on a silica instead of an alundum support. The holes through which the ends of the thermocouple and the heating element came out of the furnace were sealed with vacuum cement.

A microscope with a 32-mm. lens was mounted over the glass window in the cover, and the sample, which was placed inside the furnace, could be observed at a magnification of 35 to 40 diameters.

The only material that was investigated was a cold-rolled, ½-in. round, 0.10 per cent. carbon steel.

Even at temperatures as low as 600° C. a certain amount of rearrangement of the grain could be observed. At the beginning an instantaneous change of some grains was taking place here and there over the surface of the sample. The changes were momentary and so quick that it was impossible to see distinctly what was taking place, except that it was plain that certain grains were changing their outlines. This process progressed with an increasing intensity up to about 720° C., when a phenomenon began, to which Mr. Rogers applies the appropriate expression "wave change of microstructure." Since in the writer's case he had about 0.10 per cent. C present in the sample, this "wave" did not originate in one point, as described by Mr. Rogers, but in a number of nuclei, and progressed rather slowly from each point in all directions. This process could easily be stopped, as described by Mr. Rogers, by slightly dropping the temperature. The pearlitic islands gradually disappeared in this wave and finally could not any longer be seen.

Unfortunately, the best vacuum that could be obtained in the writer's furnace was about 0.01 mm. mercury, which is not high enough to prevent oxidation of the polished

surface of the heated sample. Consequently, simultaneously with the beginning of the grain growth, an oxide film began to be formed which hid to a certain extent the actual changes in structure. Sometimes even at 720° C. it was so heavy that the beginning of alpha to gamma transformation could not be seen. Under most favorable circumstances the disappearance of pearlite could be observed only to about half of its progress. But the completion of austenization and the complete disappearance of pearlite never could be seen. The growth of the oxide film was gradual and could easily be mistaken for the actual structural change. Only after several experiments could the difference between the two plainly be distinguished.

The formation of this film was the principle reason why under the conditions of four years ago a further investigation along this line was considered to be futile, and consequently further experiments were given up.

From his experience the writer knows that the commercial hydrogen, unless highly purified, contains sufficient foreign elements to cause oxidation of a polished iron surface at high temperatures. The writer would like to ask Mr. Rogers whether he experienced similar trouble due to the formation of oxide film, and whether he took precautions against its formation.

Mr. Rogers has broken the ground for the investigation of a broad unknown field. The visual observation of changes which take place in metals and alloys, ferrous as well as nonferrous, when subjected to high temperatures, and especially when appearance or disappearance of a phase takes place, is a fruitful and highly interesting field of research.

A. Hayes, Middletown, O.—I believe that this interesting piece of development and equipment will prove to be of very great assistance in following the spreading behavior of such coatings as vitreous, zinc, and metallic coatings on metal surfaces, where the process essentially is that of using a coating of lower melting point on the solid metal. It will offer an opportunity for making observations on spreading behaviors and spreading coefficients that thus far have not been possible. On that account it will be of considerable advantage in carrying further the investigation in the coating field.

B. A. Rogers.—I was much interested to hear of Dr. Ziegler's experiments with a furnace of similar kind. I also tried using a vacuum but the hydrogen atmosphere was so much more satisfactory that after the first heat I continued to use it. As to oxidation of the sample when using hydrogen, considerable trouble of this kind was experienced. I cannot tell exactly to what it was due, somtimes passing the hydrogen through a tube containing heated copper helped to keep down the oxidation, or what I took to be oxidation.

There seems to be considerable variation in the quality of hydrogen. Some tanks will cause no trouble at all, while it is practically impossible to work with others. I preferred to find a tank which caused no trouble rather than to try to purify the hydrogen.

*

Studies of Hadfield's Manganese Steel with the High-power Microscope

By John Howe Hall,* High Bridge, N. J.

(Henry Marion Howe Memorial Lecture†)

One's first thought, upon being chosen to deliver the Henry Marion Howe lecture, is of pride at being selected for this post of honor, but there succeeds immediately a deep sense of the obligation thereby incurred to give of one's very best in order to make a contribution worthy of him in whose memory these lectures are given. One who had the good fortune to be associated with Henry M. Howe, upon sitting down to prepare such a paper as this, immediately falls to musing upon the days when his face and his footfall were familiar from constant association, and recalls with singular vividness his active figure, his mobile, alert face, and his keenness in penetrating to the core of the subject under discussion. Like Dr. Mathews, I was a young man when I first worked under his direction, now nearly a quarter of a century ago, and in those early days he often seemed a hard taskmaster—a man whose standards it would never be possible for me to meet. I well recall his insisting upon my proving for the third time the truth of a conclusion which I had been unwilling to submit to him until it had been confirmed by two carefully planned experiments. To my impatient protest that the third demonstration he asked for was but a repetition of the second, with different samples, he replied, "Yes, that is true, but the inherent improbability of your conclusions is so evident that I can not accept them until you prove your case again." "Shall I ever do a thing well enough to suit him?" I thought.

Looking back today upon many similar incidents, I suspect that he never expected me to attain the excellence he preached, and held up to me and to himself as a model, but knew out of the fullness of his experience that in no other way could he so impress upon me the necessity in research of the patient, never-failing attention to detail and to accuracy that distinguished his own work.

How painstaking he was in the preparation of his many books and professional papers, as well as in his experimental work, was never so

---

* Metallurgical Engineer, Taylor-Wharton Iron & Steel Co.

† Presented at the New York Meeting, February, 1929.

forcefully brought home to me as when, some years after his death, I came to look over the voluminous manuscripts and proofs of his writings. Clearly, the masterly, lucid English that made it possible for us his pupils so readily to follow his most involved reasoning was attained only at the cost of hard work and great pains. How plain was the tale told by those manuscripts, with their interlineations, substitutions, and changes of the order of words in sentences, sentences in paragraphs, and paragraphs in pages! Verily, to go over those papers indicated to me as never before how, in this as in all things, he strove for perfection, and labored hard to approach it. Of his extraordinary power of coordination and of reasoning, which enabled him to bring order and sequence out of what appeared the most contradictory masses of data, many have spoken out of their personal experience, pointing for confirmation to the professional writings that are his biography and his monument.

Howe's Interest in Hadfield's Manganese Steel

From 1890 or 1891 until his death, that is for more than half of his professional career, Henry M. Howe was interested in that paradoxical metal, Hadfield's or 12 per cent. manganese steel. As the American representative of Sir Robert A. Hadfield, he brought the steel to the attention of American metallurgists, and in cooperation with Lewis H. and William J. Taylor, Oliver Chrystie, Robert E. Jennings, Maunsel White and Henry D. Hibbard he started its manufacture in America at the plant of the Taylor Iron Co., now the Taylor-Wharton Iron & Steel Co., of High Bridge, New Jersey. From 1892 until his death he served the Taylor company as consulting engineer and as vice-president, and he worked shoulder to shoulder with its officers and employees during the first critical years when manganese steel was winning its way to recognition.

My own participation in that enterprise dates from late in 1906, when I was brought to High Bridge to make metallography a recognized part of the operating routine of the shop, as had been done with chemistry a generation before. As I look today upon the photomicrographs that have succeeded the rather crude product of 1907, and read of the investigations being prosecuted with the X-ray, the high-power microscope, and other tools of modern research workers, I am moved again and again to wish that Henry M. Howe might still be with us, to lead with his lucid mind in the interpretation of the data so rapidly being accumulated. How he would have rejoiced at the deeper insight into the constitution of steel that these new instruments confer, and how delighted would he have been at the demonstration of the accuracy of some of his own conclusions, based as they were upon careful reasoning from the rather scanty data obtainable with the microscopes of 20 years ago.

Of Howe's writings on the subject of manganese steel, I wish particularly to refer to a paper read before this Institute in 1915,[1] whose title characteristically was a question—"Are the deformation lines in manganese steel twins or slip bands?"—and to several portions of his last book, "The Metallography of Steel and Cast Iron," published in 1917. In both of these places he discusses at considerable length the peculiar lines that are produced in the austenite crystals of 12 per cent. manganese steel by cold work. These lines are distinguished by the fact that they appear upon any polished and etched surface of a piece of 12 per cent. manganese steel that has been subjected to cold working previous to being cut and polished, and by the further circumstance that their abundance is in direct proportion to the amount of cold working to which the specimen has been subjected. They are brought out by various etching agents, especially by solutions of nitric acid in alcohol, and they apparently follow the cleavage lines of the austenite crystals. So well do they serve to show where one crystal ends and another begins that, when difficulty is encountered in developing clearly the crystal boundaries of a piece of 12 per cent. manganese steel, to slightly cold-work the specimen and then to repolish and etch it is a means of bringing out the structure frequently resorted to by metallographists.

It is a matter of common knowledge that 12 per cent. manganese steel hardens greatly when severely cold-worked, and that in the hardened portions these slip lines are abundant. The hardened portion, too, becomes slightly magnetic,[2] in contrast to the original, almost totally non-magnetic condition of the metal.

As a result of his observations and reasoning upon the characteristics of these lines, as revealed by the microscopes of 10 or 15 years ago, Howe concluded that they are the result of slip upon the octahedral cleavages of the austenite crystals, and that the steel immediately adjacent to the planes of slip has been transformed, at least in part, to martensite. Thus he says:[3]

> The unheated etching bands which deformation causes are shown by the accompanying hardening to represent in part martensitization with the formation of beta iron caused by slip, though, as their uniform width suggests, they may represent twinning also along the slip planes.

About three years ago, in cooperation with Francis F. Lucas, I undertook an investigation of the nature of these slip lines, as well as of some other phenomena connected with 12 per cent. manganese steel, and in this paper I shall endeavor to present some of our conclusions.

---

[1] H. M. Howe: Are the Deformation Lines in Manganese Steel Twins or Slip Bands? *Trans.*, A. I. M. E. (1915) **51**, 881.

[2] R. A. Hadfield and B. Hopkinson: *Jnl.* Iron and Steel Inst. (1914) **89**, 106.

[3] H. M. Howe: The Metallography of Steel and Cast Iron, 478.

With a few exceptions, which will be duly noted, my illustrations are all taken from Mr. Lucas' remarkable photomicrographs.

Slip Lines in Manganese Steel

In Fig. 1 is shown the microstructure with aqua regia etch of a piece of ¾-in. round rolled 12 per cent. manganese steel that has been heated to 1060° C. and quenched in water. The structure consists almost entirely of crystals of austenite, though the appearance of the grain boundaries indicates that some unabsorbed carbide may be present there. This specimen has not been subjected to any cold working, and almost no slip lines appear in the austenite grains.

Fig. 2, also etched with aqua regia, shows the structure of another sample of the same bar, which has been heated to 1060° C., quenched in water, cold-worked by pounding with a hammer, sectioned, polished, and etched. The familiar slip lines of cold-worked austenitic manganese steel are clearly in evidence, in some crystals running in but one direction, in others in two, and in still others in three.

At a magnification of 3230 dia. (reduced to 1808), as illustrated by Fig. 3, the slip lines in the cold-worked round specimen shown in Fig. 2 appear more like narrow bands of some constituent that etches differently from the main austenitic groundmass. The lines are seen to be of variable width, and to be not quite parallel with each other.

In Fig. 4 is shown the structure of a piece of thin rolled plate of 12 per cent. manganese steel, which has been heated to 1060° C., quenched in water, pounded with a hammer, sectioned, polished, etched with nitric acid, and then scratched with the microcharacter tester. By following the line traced by the diamond point, a spot has been found and photographed where the slip lines are far more abundant in certain austenite crystals than in neighboring ones. The diamond has drawn a deep furrow in the austenite that contains few slip lines but has scarcely made a mark upon the crystal that contains abundant slip lines, demonstrating that the hardness is indeed closely associated with the lines, or due to them.

Fig. 5 shows at 3230 dia. (reduced to 1808) the structure of the specimen illustrated in Fig. 1, but etched with boiling sodium picrate. The boundaries of the austenite crystals, with faint traces of slip lines here and there, are all that appear. The cold-worked specimen illustrated in Figs. 2 and 3, when etched with boiling sodium picrate, shows at 3230 dia. (reduced to 1808) the structure illustrated in Fig. 6, in which the slip lines are outlined by some substance that etches black. The thin plate illustrated in Fig. 4, when etched with boiling sodium picrate, and magnified 3230 dia. (reduced to 1808), as in Fig. 7, contains even more abundant evidence of the presence of a constituent in the slip lines that etches black. That this constituent is carbide in

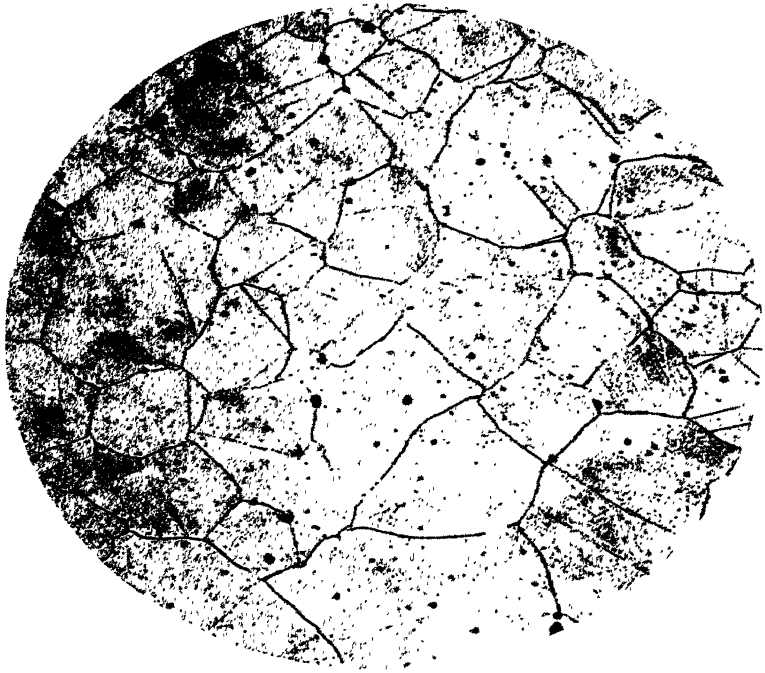


FIG. 1.—AQUA REGIA ETCH. × 265.

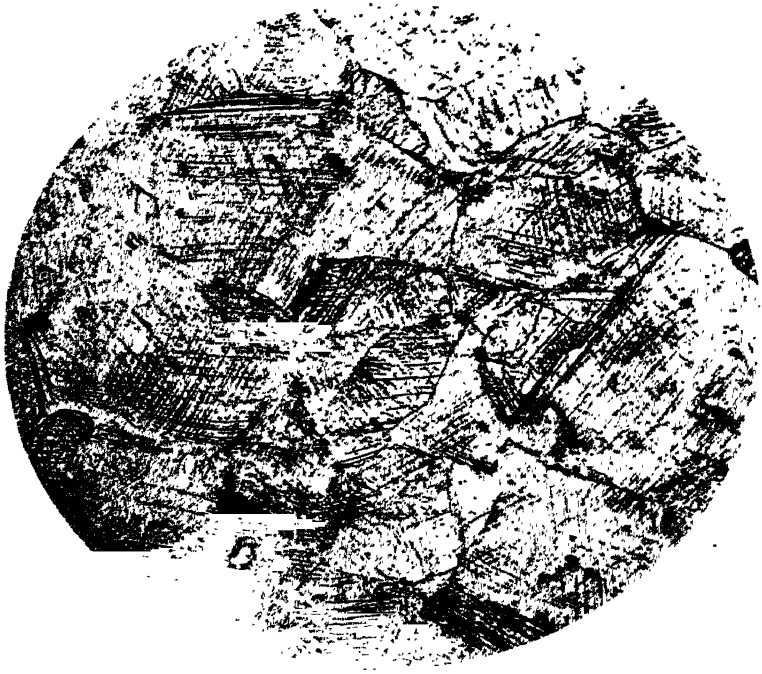


FIG. 2.—AQUA REGIA ETCH. × 265.
(Figs. 1 and 2 both reduced 56 per cent., original magnification given.)

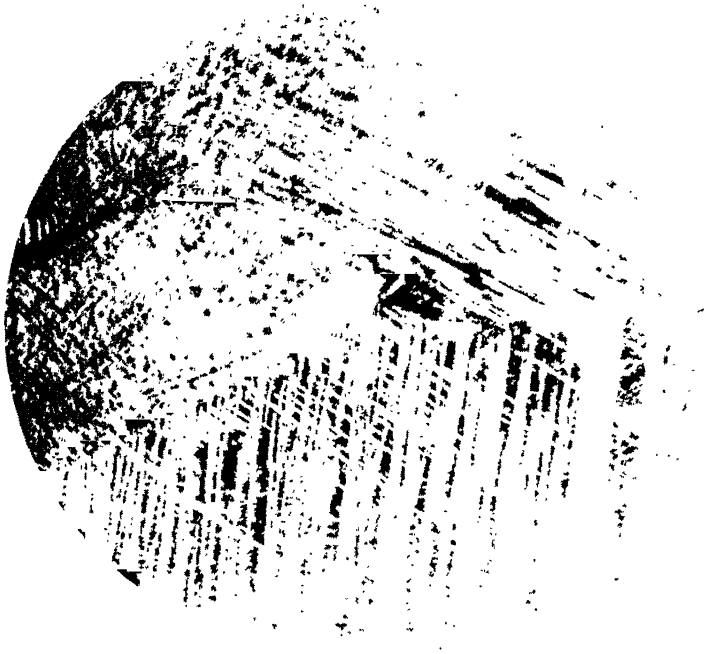


FIG 3.—AQUA REGIA ETCH. × 3230.

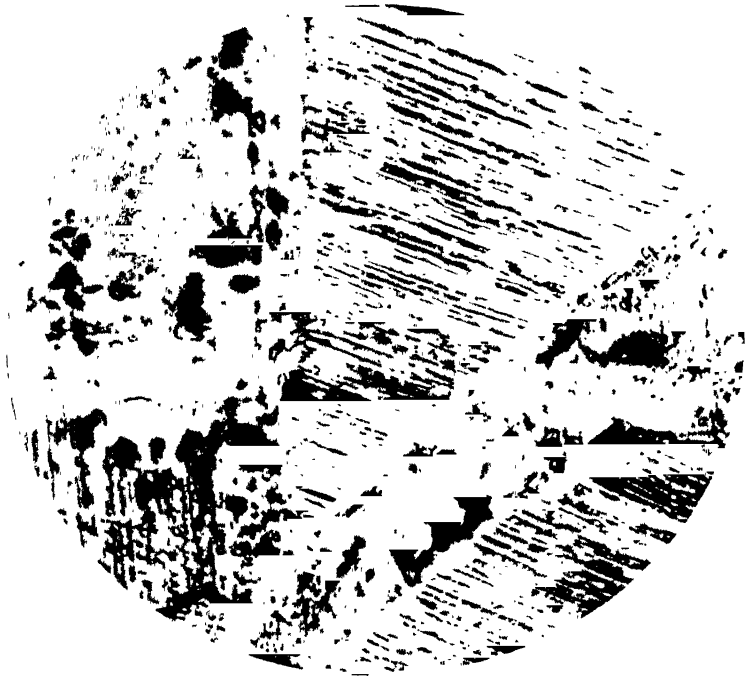


FIG. 4.—NITRIC ACID ETCH. × 3230.
(Figs. 3 and 4 both reduced 56 per cent., original magnification given.)

FIG. 5.—SODIUM PICRATE ETCH. × 3230.

FIG. 6.—SODIUM PICRATE ETCH. × 3230.
(Figs. 5 and 6 both reduced 56 per cent, original magnification given.)

a finely divided state, there appears to be very little doubt. Certainly the black particles are not pits, as is shown by examination of Fig. 8. This shows the structure of a piece of the ¾-in. round rolled 12 per cent. manganese steel, heated to 1060° C., quenched in water, pounded with a hammer, sectioned, polished, etched with boiling sodium picrate, and then scratched with the microcharacter tester. The diamond point has dragged along some of the black-etching constituent, as is clearly seen near one end of the scratch, which it would not do were these spots pits.

Potassium bitartrate is known to be an etching agent that blackens alpha iron, and the round specimens already described were repolished and etched with this reagent. Fig. 9 shows the unworked specimen and Fig. 10 the cold-worked one, at 265 dia. (reduced to 148), etched with potassium bitartrate. The absence of the slip lines in the unworked specimen, and their abundance in the cold-worked one, is clearly brought out, and illustrated even better in Fig. 11, showing the cold-worked specimen magnified 3500 dia. (reduced to 1960). The close resemblance between Figs. 3, 4, and 11 is most striking.

We have shown, then, that the slip lines are brought out clearly by a reagent that darkens carbides and by one that darkens alpha iron. That both the carbides and the alpha iron are in a finely divided condition is evident from a careful examination of the photomicrographs. I do not propose to consider in detail the views held by different metallurgists as to the exact nature of martensite. Professor Sauveur has done that in a recent paper[4] presented before this Institute, in which he showed that the majority of metallurgists believe what we have long called martensite to be some sort of a mixture of carbide and alpha (or, at least, non-gamma) iron, in a finely divided state. The evidence indicates that the material in the slip lines of cold-worked 12 per cent. manganese steel corresponds to this definition, or in other words it is, as Howe concluded, martensite.

If in the cold-worked material an appreciable amount of martensite exists, the specific gravity of a thin specimen should be less after severe cold working than before. A small piece of the thin sheet already described was found to have a specific gravity of 7.9305 after quenching in water from 1060° C., and of 7.9226 after the same treatment followed by severe pounding with a hand hammer, which bears out the evidence of the photomicrographs. The same fact was noted by Hadfield and Hopkinson.[5]

Finally, E. C. Bain kindly consented to examine with the X-ray spectrometer specimens of ¾-in. round rolled manganese steel after

[4] A Sauveur: Current Theories of the Hardening of Steel Thirty Years Later. *Trans.*, A. I. M. E. (1926) **73**, 859.

[5] R. A. Hadfield and B. Hopkinson: *Loc. cit.*

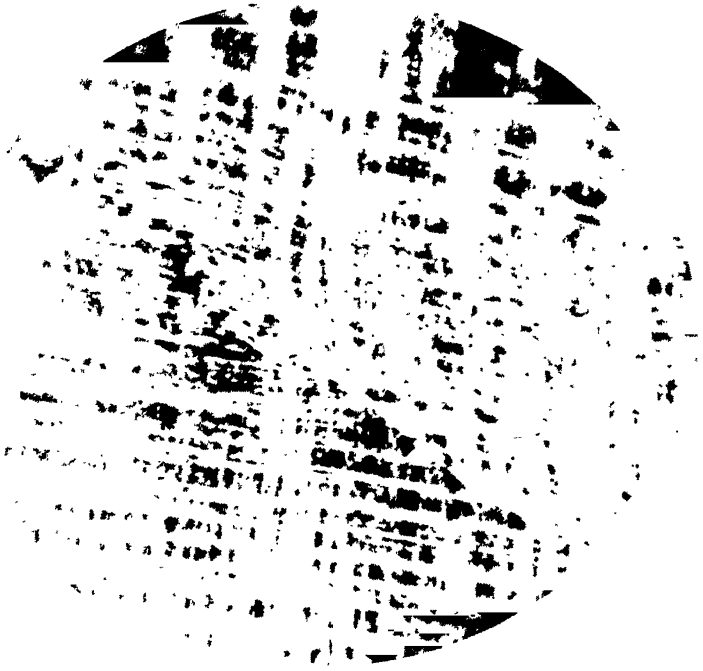


FIG. 7.—SODIUM PICRATE ETCH. × 3230.

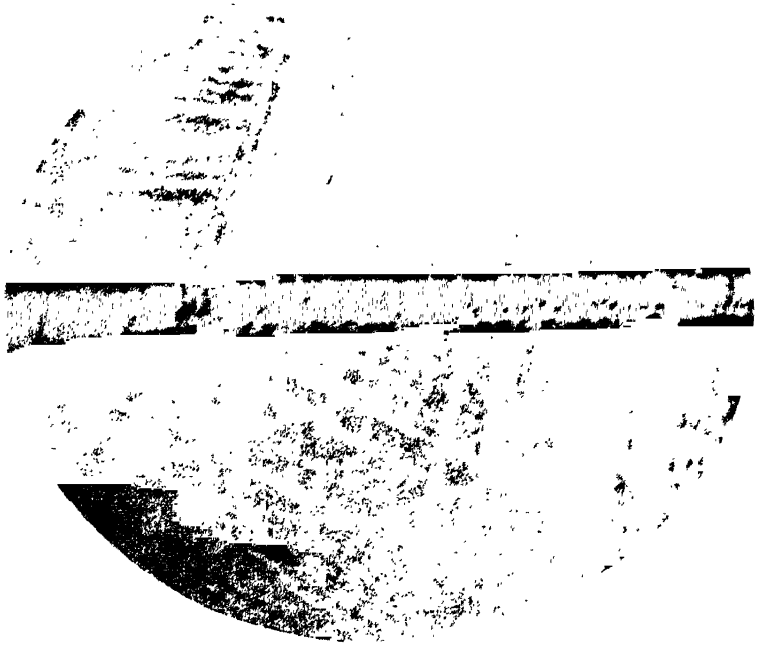


FIG. 8.—SODIUM PICRATE ETCH. × 3230.
(Figs. 7 and 8 both reduced 56 per cent., original magnification given.)

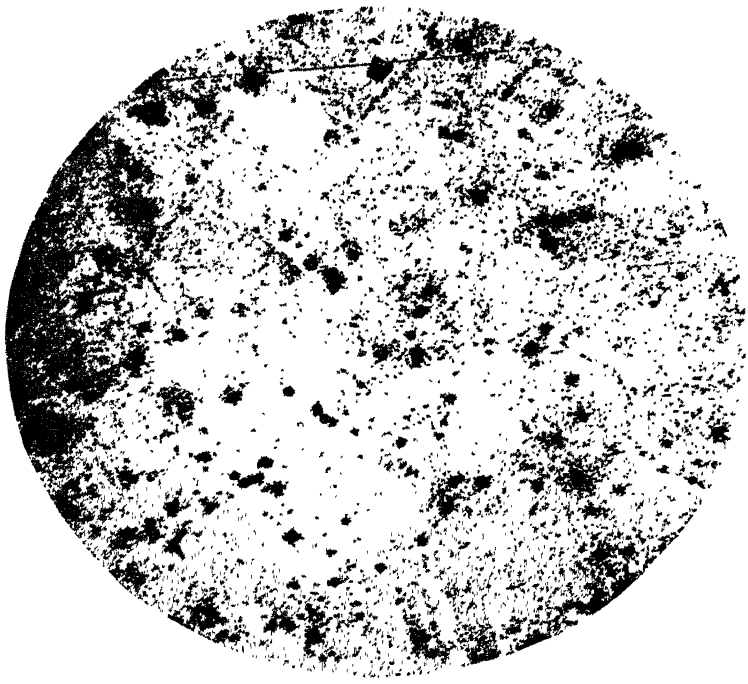


FIG. 9.—POTASSIUM BITARTRATE ETCH. × 265

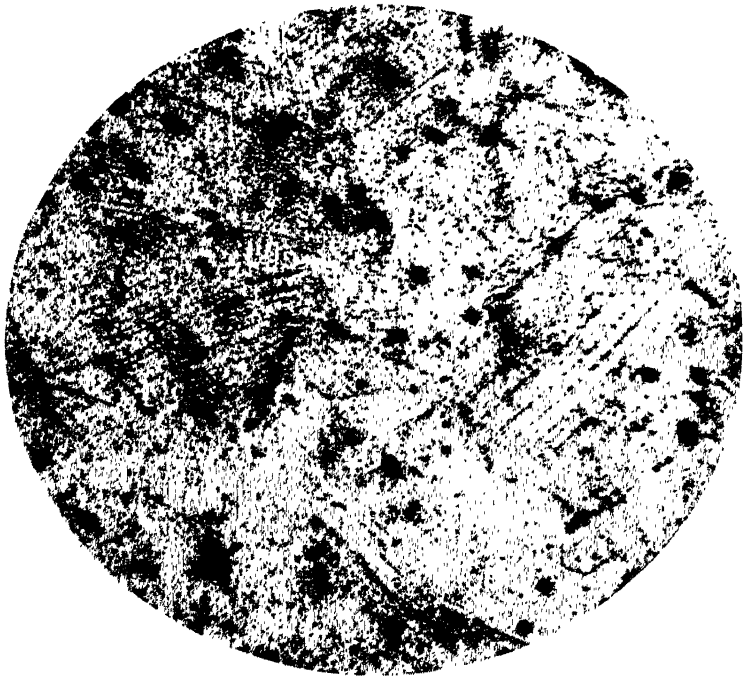


FIG. 10.—POTASSIUM BITARTRATE ETCH. × 265.
(Figs. 9 and 10 both reduced 56 per cent., original magnification given.)

quenching in water from 1060° C., and after this same treatment followed by cold working with a hammer. This work was done in the research laboratories of the Union Carbide and Carbon Corpn., with which Mr. Bain was then associated.

Both the cold-worked samples and those that were not cold worked were warmed to about 200° C. before exposure to the X-rays, in order to improve the contrast of the alpha iron lines by rendering them narrower and less diffuse. The same general effect is produced also in the marten-

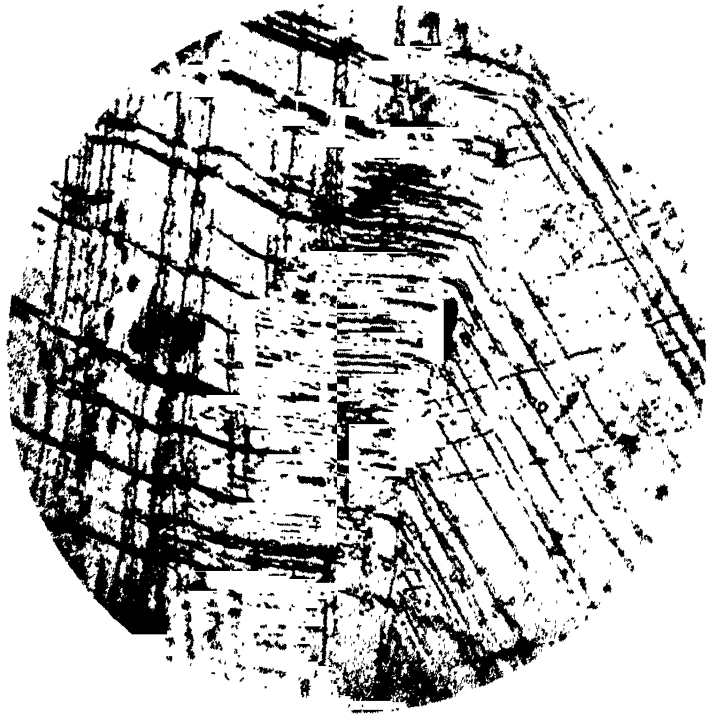


FIG. 11.—POTASSIUM BITARTRATE ETCH. × 3500.
(Reduced 56 per cent., original magnification given.)

site of any low-alloy steel. In the specimens that were not cold worked Mr. Bain found only the characteristic lines of gamma iron, but in the cold-worked material fairly well marked alpha iron lines could be detected also. Fig. 12 shows the X-ray crystallograms of the worked and unworked material, with that of ferrite placed alongside for comparison. The crystallogram of the unworked manganese steel is at the top, marked "austenite," that of ferrite at the bottom, and that of the cold-worked manganese steel in the center. Some of the alpha iron lines are visible in the crystallogram of the cold-worked manganese steel. Mr. Bain writes as follows:

"The atomic arrangement in all gamma iron and its solid solutions is quite different from that in ferrite. Accordingly their X-ray diffraction patterns are radically different and constitute absolute quantitative tests for the two allotropic forms of iron and iron solid solutions. In general, however, the X-ray diffraction pattern produced by a very small amount of one constituent in a large amount of another does not serve as a very delicate test even though it is extremely characteristic.

"In Fig. 12 the pattern marked *A* is of essentially pure austenite—Hadfield's manganese steel. The pattern marked *C* is of pure ferrite. The pattern *B* is of the material *A* after severe cold work, sufficient to raise the Rockwell *C* hardness to a value of 50 from about 10 in the original condition. This cold work brought about an increase in the force of

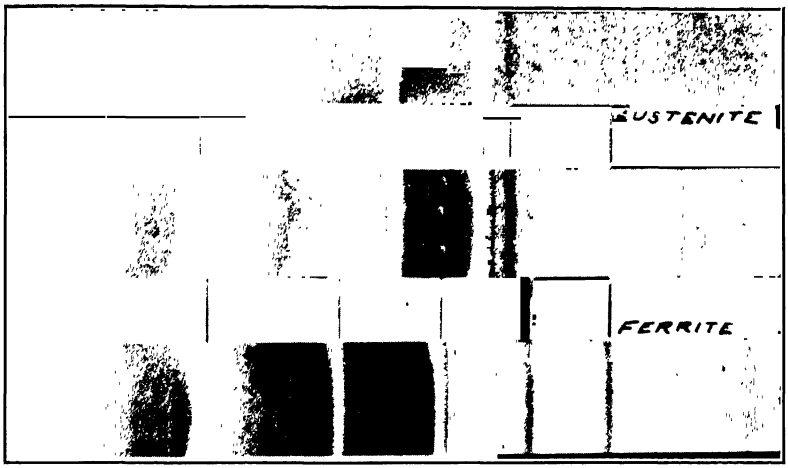


FIG. 12.—X-RAY SPECTROGRAMS; WORKED AND UNWORKED MANGANESE STEEL

attraction to a small magnet of about 200 per cent. It will be observed that some faint, though definite, new lines were added to the X-ray diffraction pattern by cold work. These lines can be exactly identified as being those of alpha iron or ferrite. The intensity of these lines is perhaps only about one one-hundredth that of the gamma iron lines of the same sample, and consequently the amount of iron transformed by the cold work could not be more than 1 or 2 per cent.

"It is only by the rarest good fortune in choosing the duration of exposure to X-rays and in the contour of the specimen and the technique of printing the crystallogram that the lines can be made visible at all. The particular films shown here are the result of many trials. The first three ferrite lines are all that usually were visible, superimposed on the austenite pattern, but in one case four lines could be observed in the original films."

Had such photographs as these been available, Howe would hardly have given the uniform width of the lines as a possible indication that they are due to twinning. In Fig. 3, for instance, and in many others of our pictures, the width of the lines varies considerably. It is noticeable, too, in most of the figures that the lines do not zigzag each other, as they would were they areas of twinning. Only in Fig. 11 is there noticeable zigzagging of the lines by other lines, and even in that picture not all the lines so transpose each other. We are brought back, then, to Howe's principal conclusion that the lines represent martensitization along planes of slip, and are led to applaud the accuracy of his reasoning, based as it was on photographs that gave hardly an indication of the true nature of these lines.

Dendritic Structure in 12 Per Cent. Manganese Steel

In 1924, Prof. Albert Sauveur and Dr. V. N. Krivobok presented a paper[6] on the use of sodium picrate in revealing dendritic segregation in iron alloys, in which they showed some excellent examples of dendritic structures in cast 12 per cent. manganese steel. Opinions as to the effect of dendritic structures upon the properties of metals have varied widely. Without pretence of giving an answer to this question, I shall show several photomicrographs bearing on the subject, and later will give the results of some physical tests of manganese steel that throw some light upon the effect of the dendritic structure.

Fig. 13, at 400 dia. (reduced to 224), shows the structure of a bar of manganese steel, ½ by ¾ in. cross-section and 12 in. long, containing carbon 1.24 per cent., silicon 0.62 per cent., manganese 12.3 per cent., in the cast condition, before any heat treatment except cooling naturally from the liquid state. This specimen was etched with picric acid, which reveals the carbide network between the austenite crystals, a few larger patches of carbide, and a certain uneven appearance of the austenite crystals, suggestive of inequalities of composition.

At the same magnification, but etched with boiling sodium picrate, this specimen is shown in Fig. 14, in which the boundaries of the austenite grains appear as heavy black lines and the segregated carbides as black spots. This etching shows also strongly marked dendrites, which in some cases conform to the outline of the austenite crystals and in other cases do not.

Fig. 15, the same specimen with boiling sodium picrate etch, magnified 2450 dia. (reduced to 1225) shows that the dendritic structure in many places ignores the boundaries of the crystals, which intersect the dendrites in a haphazard manner.

[6] A. Sauveur and V. N. Krivobok: Use of Sodium Picrate in Revealing Dendritic Segregation in Iron Alloys. *Trans.*, A. I. M. E. (1924) **70**, 239.

FIG. 13.—PICRIC ACID ETCH. × 400.
(Reduced 56 per cent., original magnification given.)

FIG. 14.—SODIUM PICRATE ETCH. × 400.

FIG. 15.—SODIUM PICRATE ETCH. × 2450.
(Reduced 50 per cent., original magnification given.)

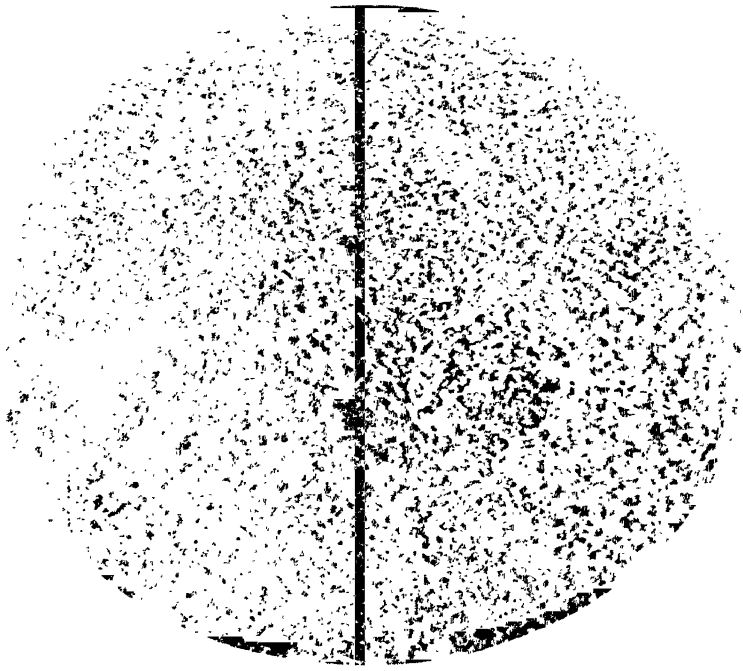


FIG. 16.—NITRIC ACID ETCH. × 50.
(Reduced 56 per cent., original magnification given.)

Another bar, of the same size and analysis as that shown in Figs. 13, 14, and 15, was heated at one end to 1060° C. for several minutes, the other end being kept cold, and was then quenched in water. The fact that some carbides remained at the hot end indicates that the actual temperature reached must have been a little below 1060° C. The bar was split longitudinally, with a thin abrasive wheel under a stream of water, from the hot end to the point where red color had disappeared when the bar was hot It was then cut into short lengths, which were polished and appropriately etched. From a series of pictures taken along this specimen, several have been selected that illustrate the characteristic appearance of the different portions. These photomicrographs have been magnified only 50 dia. (reduced to 28), in order to bring out the dendritic structures more closely.

Fig. 16, etched with nitric acid, was taken at a point close to where the bar was at a "black heat." The austenite crystals, with carbides separating them, and distributed throughout their area, are typical of the untreated steel.

Fig. 17, also etched with nitric acid, was taken at a point where the steel was at a dark red heat, so that some of the carbide had been taken into solution in the austenite. The marked dendritic arrangement of the carbide is especially noticeable, and here again it will be seen that the dendrites do not always conform to the boundaries of the austenite crystals.

At the hot end of the bar, where most of the carbide has been absorbed, the structure is shown in Fig. 18, etched with nitric acid. Some carbides are present, which would not be so had the bar actually been heated to 1060° C. and held at that temperature for 10 or 15 minutes. No tendency to dendritic arrangement of the carbides is traceable in this photomicrograph.

The same specimens, repolished and etched with boiling sodium picrate, are shown in Figs. 19, 20, and 21. Fig. 19 is taken at nearly the same point as Fig. 16, close to where the color died out when the bar was hot. The strongly marked dendritic pattern is most striking, and it persists throughout the length of the bar, as will be seen in Fig. 20, taken quite close to the hot end, and in Fig. 21, taken at the hot end.

It will be apparent that at the hot end of the bar the dendrites are less well marked than in the untreated material, where the uneven distribution of the carbides has not been modified by heating. The dendrites, however, have not completely disappeared. In our experience they seldom are entirely absent in manganese steel, even after careful heat treatment. Naturally, the dendrites are much more in evidence in 12 per cent. manganese steel that has been cast very "hot" than in pieces poured from metal that has cooled nearly to its freezing point, and generally they are also larger in the "hot-poured" metal. The evi-

FIG. 17.—NITRIC ACID ETCH. × 50.

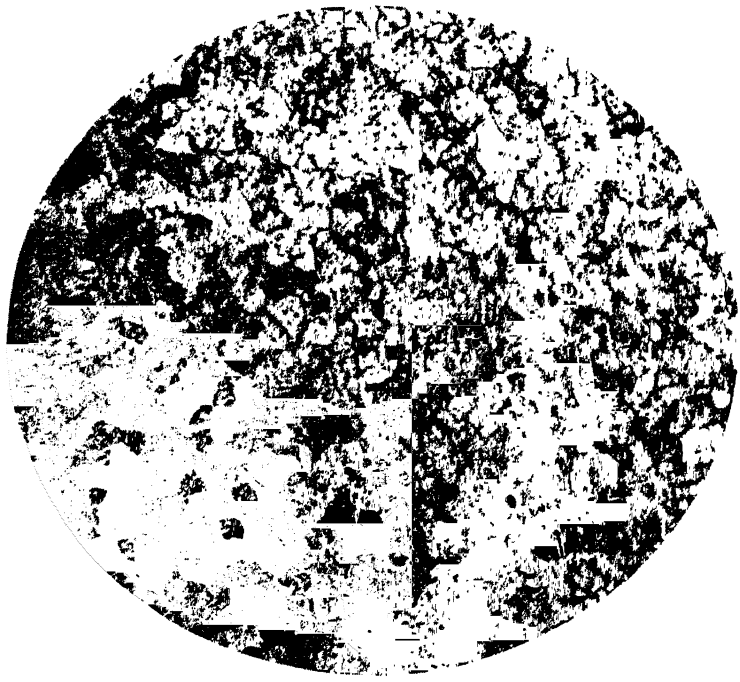


FIG. 18.—NITRIC ACID ETCH. × 50.
(Figs. 17 and 18 both reduced 56 per cent., original magnification given.)

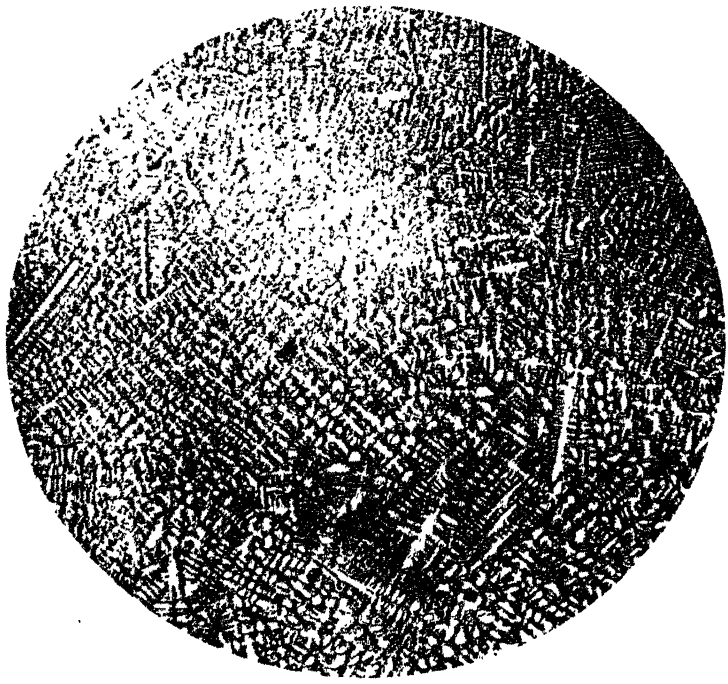


FIG. 19.—SODIUM PICRATE ETCH. × 50.

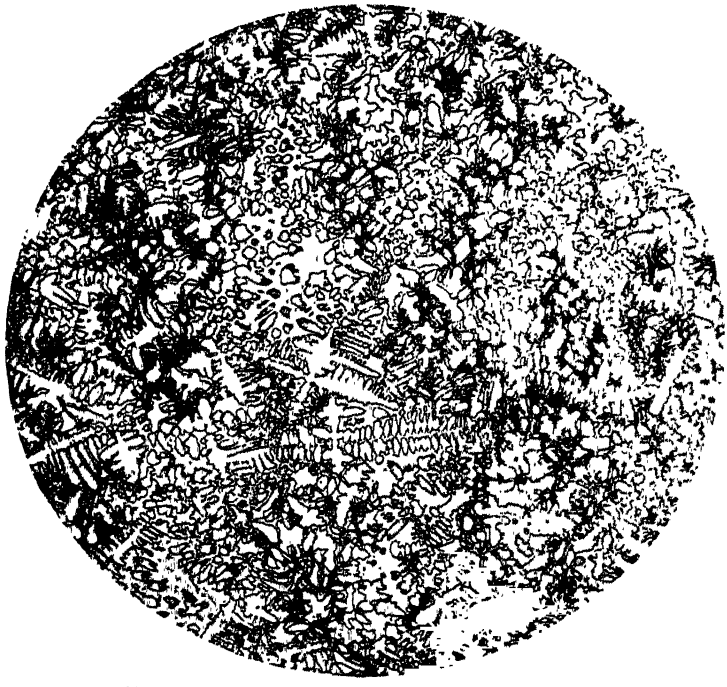


FIG. 20.—SODIUM PICRATE ETCH. × 50.
(Figs. 19 and 20 both reduced 56 per cent., original magnification given.)

dence indicates that the dendritic structure of 12 per cent. manganese steel is largely due to the uneven distribution of the carbides, which were concentrated in the fillings of the dendrites when the steel solidified and have not had time in the usual heat treatment process to become completely diffused through the austenite crystals.

A little later, in discussing another phase of my subject, I shall show several other examples of dendritic structure, and some physical tests which lead me to suspect that, in 12 per cent. manganese steel at least, these structures have very little influence on the physical properties of the metal.

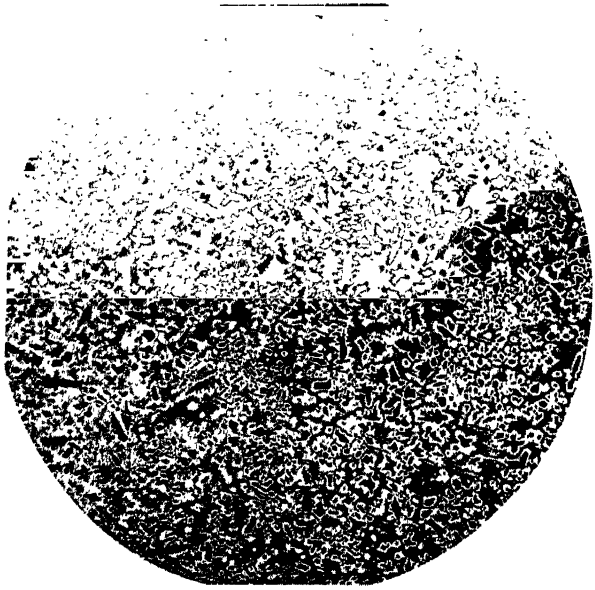


FIG. 21.—SODIUM PICRATE ETCH. × 50.
(Reduced 56 per cent., original magnification given.)

"PEARLITIC THREADS" IN 12 PER CENT. MANGANESE STEEL

The specimen taken from the point on the taper heated bar, where the metal had been heated to a dark red, shown at 50 dia. (reduced to 28) in Fig. 17, when etched with nitric acid and magnified 3500 dia. (reduced to 1960), is found to present the appearance illustrated in Figs. 22 and 23. In Fig. 22 the focus is on the carbides, whose characteristic arrangement is clearly shown, while in Fig. 23 the carbides, which stand slightly in relief, are out of focus, and the microscope is correctly focused to bring out the peculiar zebra markings of the austenite. Fig. 24 shows the same structure at 3500 dia. (reduced to 1960), at a point close to Figs. 22 and 23, but where only small spots of carbide are in evidence. This specimen also was etched with nitric acid, and the zebra striped appearance of the austenite is again in evidence.

FIG. 22.—NITRIC ACID ETCH. × 3500.

FIG. 23.—NITRIC ACID ETCH. × 3500.
(Figs. 22 and 23 both reduced 56 per cent., original magnification given.)

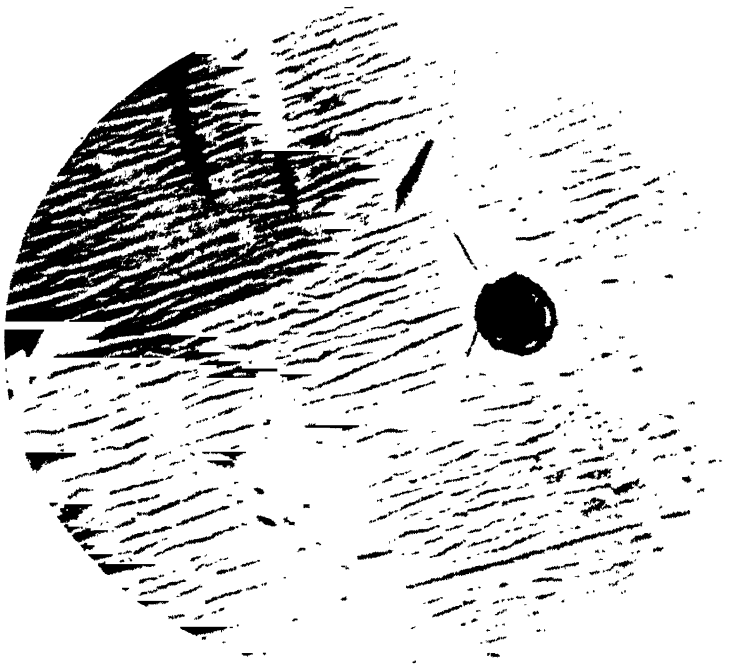


FIG. 24.—NITRIC ACID ETCH. × 3500.

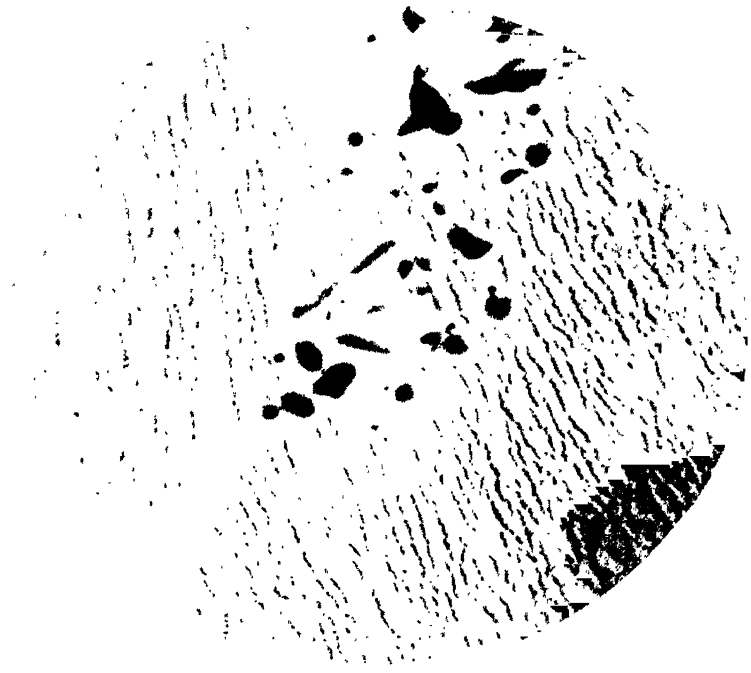


FIG. 25.—NITRIC ACID ETCH. × 3500.
(Figs. 24 and 25 both reduced 56 per cent., original magnification given.)

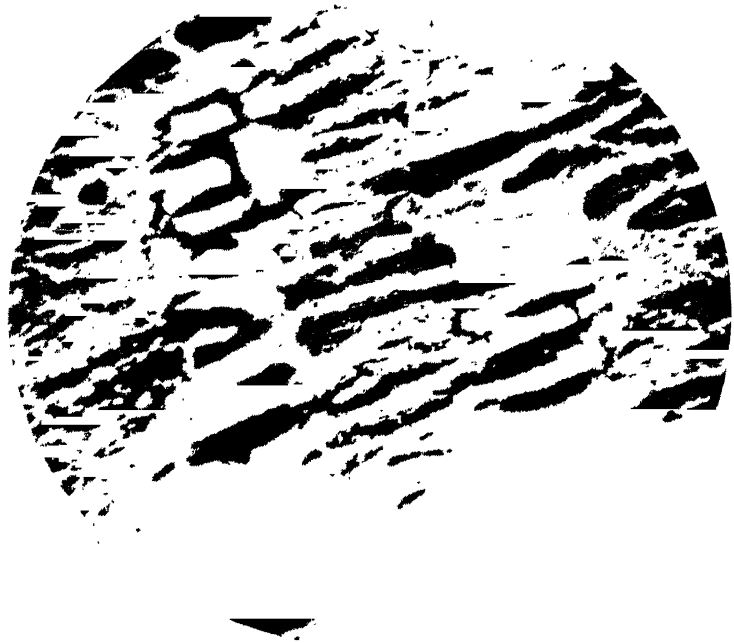


FIG. 26.—DEEP NITRIC ACID-SODIUM PICRATE ETCH. × 2450.

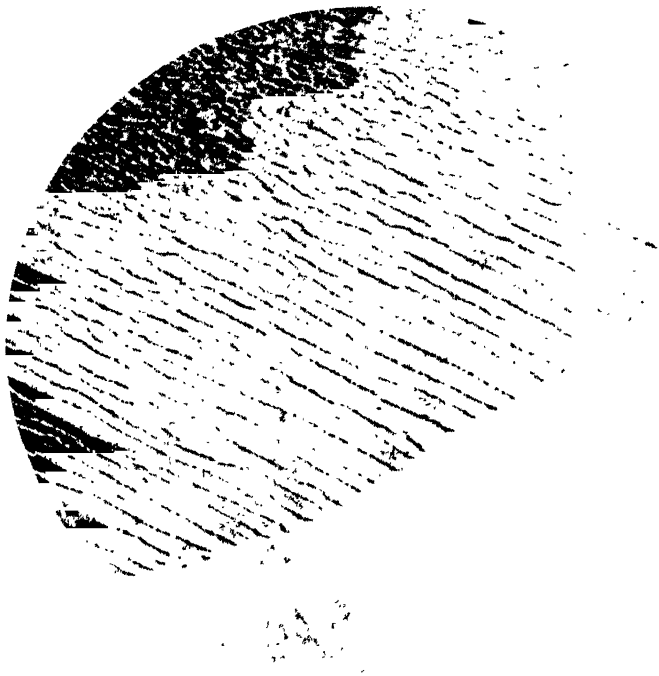


FIG. 27.—NITRIC ACID ETCH. × 3500.
(Figs. 26 and 27 both reduced 56 per cent., original magnification given.)

Fig. 25 at 3500 dia. (reduced to 1960), etched with nitric acid, shows the same structure near a small patch of remanent carbides in a ¾-in. square bar of cast manganese steel containing 1.23 per cent. carbon, 12.7 per cent. manganese, which has been heated to 1060° C. and quenched in water. Evidently the bar was not maintained at maximum temperature quite long enough to absorb all the carbides.

Etching with boiling sodium picrate, even for as long as 27 min., failed to develop these peculiar white stripes in any of the specimens examined. The stripes, therefore, do not consist of carbides, even in a finely divided condition, for were they carbides they would of course stain black, or at least dark brown, when etched with boiling sodium picrate.

The same area as that shown in Figs. 22 and 23 was repolished and etched deeply with nitric acid to bring out these white lines, then etched again with sodium picrate to darken the carbides and bring out the dendritic structure of the metal. The appearance of the steel after this etching is shown at 2450 magnifications (reduced to 1372) in Fig. 26. Here are illustrated the axes of several dendrites and the fillings between them. The white lines are broader and better marked in the fillings than in the axes of the dendrites.

These lines persist in the steel in which the carbides have been absorbed by proper heat treatment, as is shown by Fig. 27, a view at 3500 dia. (reduced to 1960), with nitric acid etch, of a portion near the hot end of the taper heated bar shown in Figs. 16 to 24. The white lines in this specimen stop at the boundary of an austenite grain, and in the neighboring grain are seen round dots which look like the cross-sections of another set of lines, differently oriented. This and a number of similar illustrations in our possession lead us to suppose that these lines lie in the cleavages of the austenite, not as continuous plates, but as threads, so that a section parallel to their greatest dimension shows them as lines, while in a cross-section they appear as dots.

In Fig. 28 are shown similar lines in a specimen cut from a 3-in. square bar of cast manganese steel containing carbon 1.22 per cent., manganese 13.0 per cent., silicon 0.68 per cent., which has been heated to 1060° C. and quenched in water. This photomicrograph is magnified 3500 dia. (reduced to 1960), the etch being nitric acid. Though there is apparently no carbide whatever in the boundary between the two austenite crystals, parts of which are shown, the white lines cease abruptly at this crystal boundary and the direction of the lines in the two crystals is quite different.

A small piece of manganese steel of the same composition as that shown in Fig. 25 was heated to 1060° C. for 2 hr. and quenched in iced brine, in an effort to see if prolonged heating and very rapid quenching, which will completely eliminate carbides from the microstructure, would

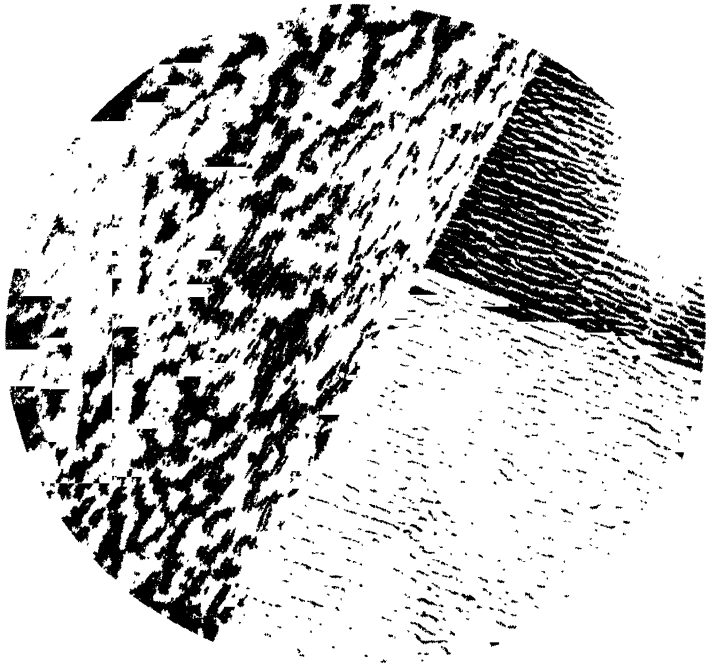


FIG. 28.—NITRIC ACID ETCH. × 3500.

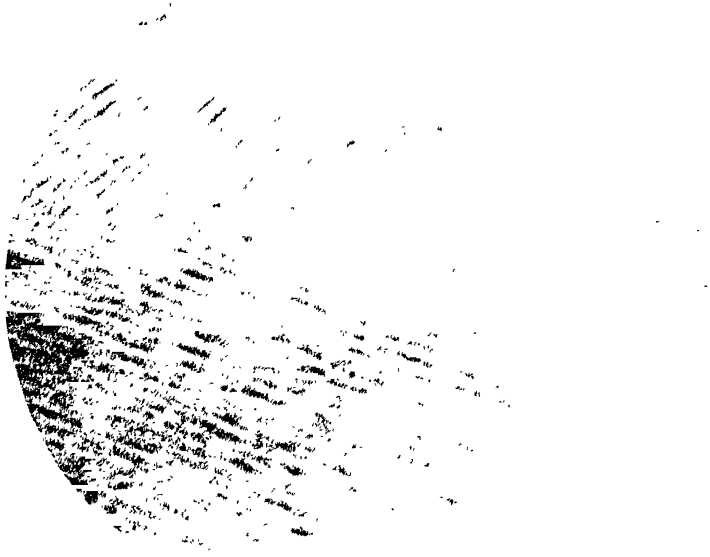


FIG. 29.—NITRIC ACID ETCH. × 3500.
(Figs. 28 and 29 both reduced 56 per cent., original magnification given.)

wipe out also these peculiar white lines, or threads, as perhaps they had better be called. Fig. 29 shows this specimen, etched with nitric acid, and magnified 3500 dia. (reduced to 1960). Portions of four austenite crystals are included in the plate, each with a differently oriented set of the white threads.

The evidence, then, is that these threads are most pronounced in the steel that has had little or no heat treatment to cause the absorption of the carbides, that they are not themselves composed of carbide, that they are widest in the fillings of the dendrites, and that in the steel in which the carbide has been entirely absorbed by heat treatment they are still present, though much less marked than in the untreated material.

Emulating one of my predecessors in the position of Howe lecturer, I shall say that I am not myself satisfied as to the meaning of these threads. Mr. Lucas suggests that they represent the paths along which carbides move in disseminating into the austenite as the steel is being heated, or in leaving the austenite and gathering into segregated masses during comparatively slow cooling of the metal. The slight differences in carbon content between these paths of carbon migration and the immediately adjacent metal, he suggests, cause the threads to appear when the steel is examined under high-power magnification, after etching with nitric acid. Like Henry M. Howe, in the paper referred to earlier, the title of which was a question, I shall close this portion of my paper by asking, "Are the white lines or threads in 12 per cent. manganese steel paths of carbide migration?"

Effect of Annealing 12 Per Cent. Manganese Steel at Low Temperatures

In the paper by Hadfield and Hopkinson already referred to, the effect of prolonged annealing at low temperatures upon the physical and magnetic properties of 12 per cent. manganese steel is discussed at length. In particular, it is there shown that by annealing for many hours at temperatures of from 450° C. to 600° C., manganese steel can be made to possess nearly 60 per cent. of the specific magnetism of pure iron. At the same time its hardness is greatly increased and it becomes extremely brittle. Upon taking heating curves of this annealed material, a well marked critical point is found at about 700° C., and at or near this temperature the magnetism acquired during the previous long heating disappears. Unfortunately, the photomicrographs accompanying the paper give little or no explanation of the causes of the facts observed.

In Figs. 30, 31, 32 and 33 are shown the structure of a piece of ¾-in. round rolled manganese steel, which has been heated to 1060° C., quenched in water, again heated for 25 hr. at 500° C., and finally cooled in air. The Brinell hardness of the steel is 415; before the prolonged heating the hardness was between 180 and 200. Fig. 30 shows this

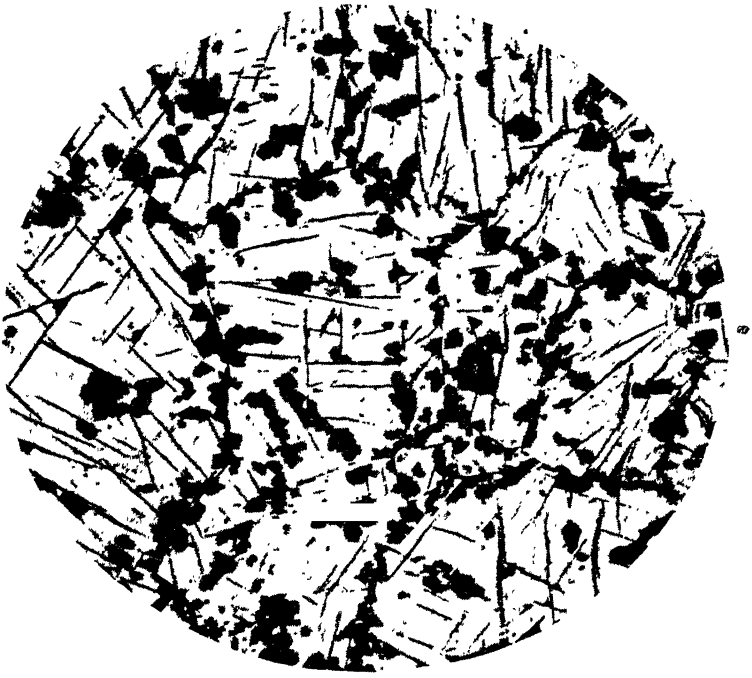


FIG. 30.—PICRIC ACID ETCH. × 540.

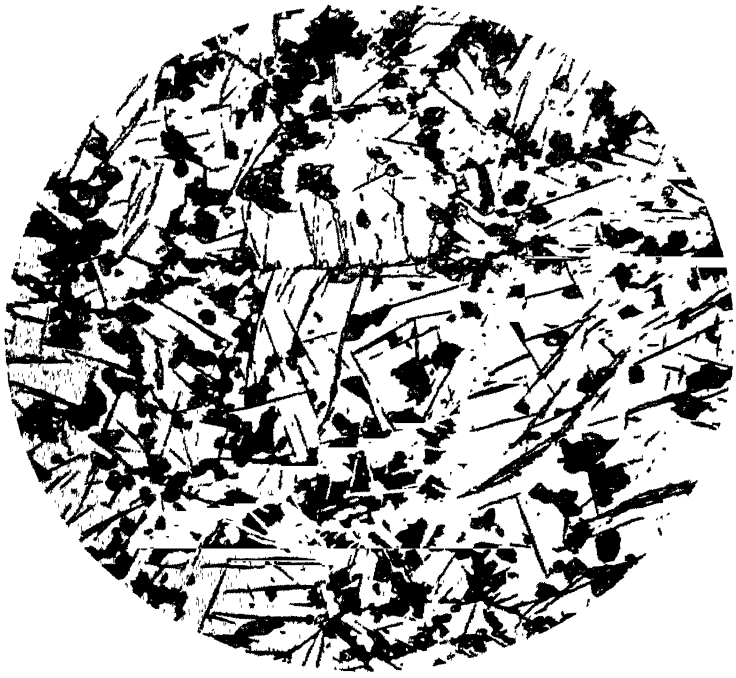


FIG. 31.—SODIUM PICRATE ETCH. × 540.
(Figs. 30 and 31 both reduced 50 per cent., original magnification given.)

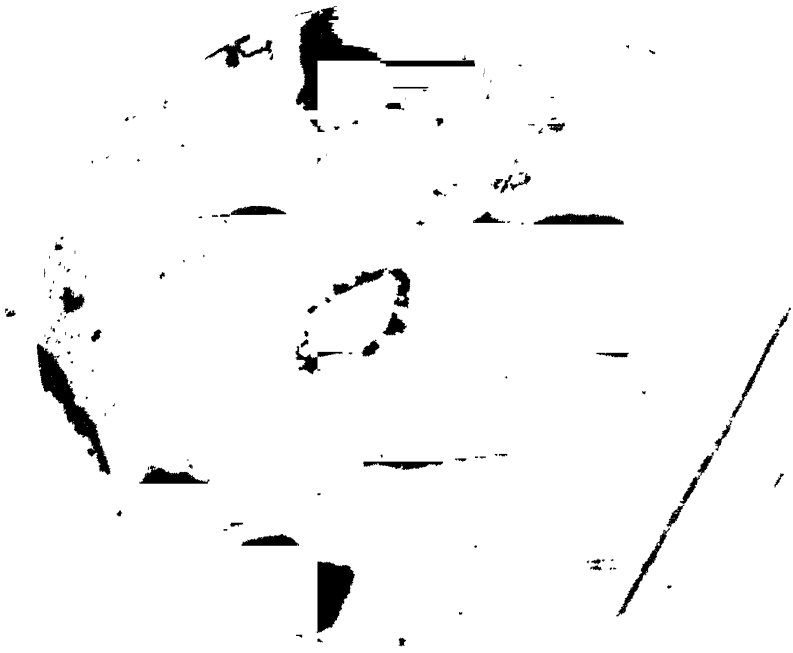


FIG. 32.—PICRIC ACID ETCH. × 4400.
(Reduced 50 per cent., original magnification given.)

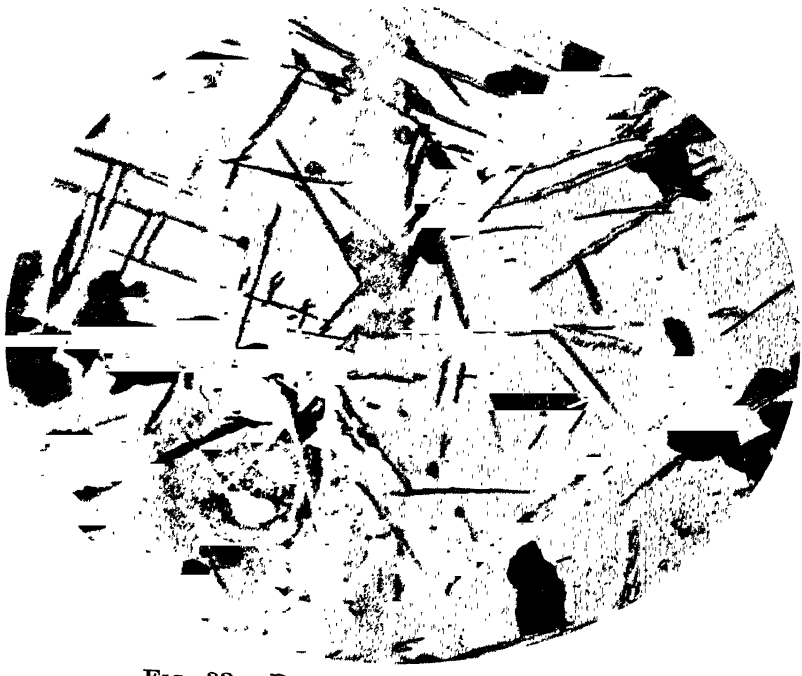


FIG. 33.—PICRIC ACID ETCH. × 2440.
(Reduced 56 per cent., original magnification given.)

specimen at 540 dia. (reduced to 270), with picric acid etch, the structure consisting of austenite with needles and veins of carbide and patches of troostite. Fig. 31 shows the same specimen at the same magnification but etched with boiling sodium picrate, which has stained the carbide needles and patches black, while the troostite areas are gray. Etched with picric acid and magnified 4400 dia. (reduced to 2200), the same specimen is found to contain areas of troostite, as illustrated in Fig. 32, in which the beginning of the development of pearlite is clearly apparent.

The microcharacter tester, when applied to this specimen, scratches the austenite quite deeply, but merely wipes off the etch from the troostite patches, as is illustrated by Fig. 33, which shows this same specimen etched with picric acid and magnified 2440 dia. (reduced to 1366).

It is evident from these photomicrographs that the prolonged heating at 500° C. has brought about a transformation of part of the austenite of the manganese steel to troostite, or troostite mixed with martensite, and even to pearlite. Like the effect of quenching in suppressing the transformation in carbon steel, the effect of manganese in these steels is normally to prevent transformation of the austenite at all ordinary rates of cooling, though carbide is liberated on cooling in crossing the S. E. line, just as it is in carbon steels. Increasing the pressure, as it were, that tends to bring about transformation, as for instance by immersion in liquid air, does not cause transformation of the austenite of 12 per cent. manganese steels. On the other hand, if the resistance to transformation is decreased, or, better perhaps, if more time is allowed for transformation to occur, by holding the steel for many hours at a temperature below its transformation point, partial transformation does take place. Could the steel be cooled from a high temperature at an exceedingly slow rate, the same thing would undoubtedly occur, and sufficiently delicate apparatus, were such in existence, would almost certainly detect a critical point in cooling, probably a little below the well marked critical point found by Hadfield and Hopkinson at 700° C. on heating this partly transformed steel.

The next question that occurs to one's mind is what happens when manganese steel that has been partly transformed by long heating is again heated above the critical point just described. In Figs. 34 and 35 are shown the structures of the same specimen from which Figs. 30 to 33 were taken, after again heating to 750° C. for 1 hr. and quenching in water. Fig. 34 shows this specimen etched with picric acid and Fig. 35 the same piece etched with boiling sodium picrate, both magnified 3500 dia. (reduced to 1960). The areas that were troostitic after the long annealing at 500° C. are seen to have been changed to aggregations of carbides by a further heating at 750° C. The alpha iron that was associated with the carbide after annealing at the lower temperature, and which gave the metal its magnetic properties, has been reabsorbed into

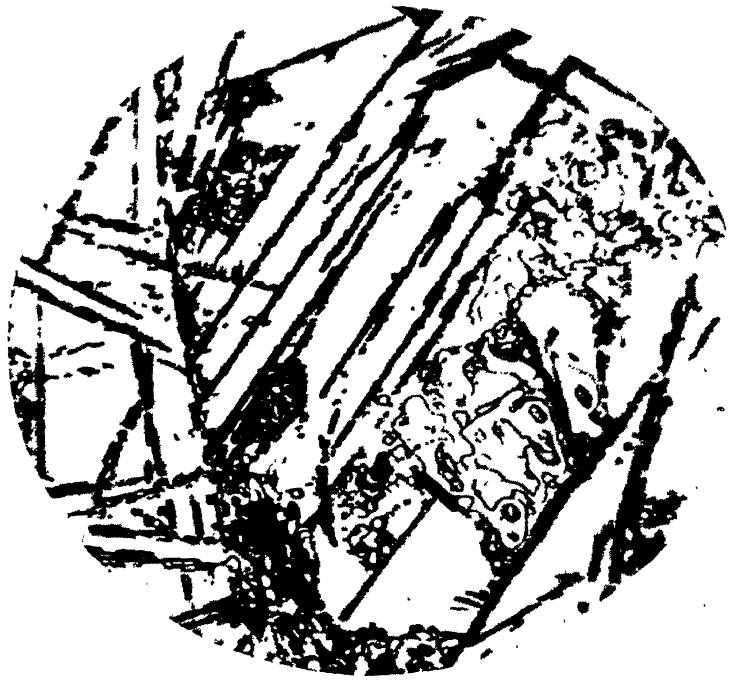


FIG 34.—PICRIC ACID ETCH. × 3500.

FIG. 35.—SODIUM PICRATE ETCH. × 3500.
(Figs. 34 and 35 both reduced 56 per cent., original magnification given.)

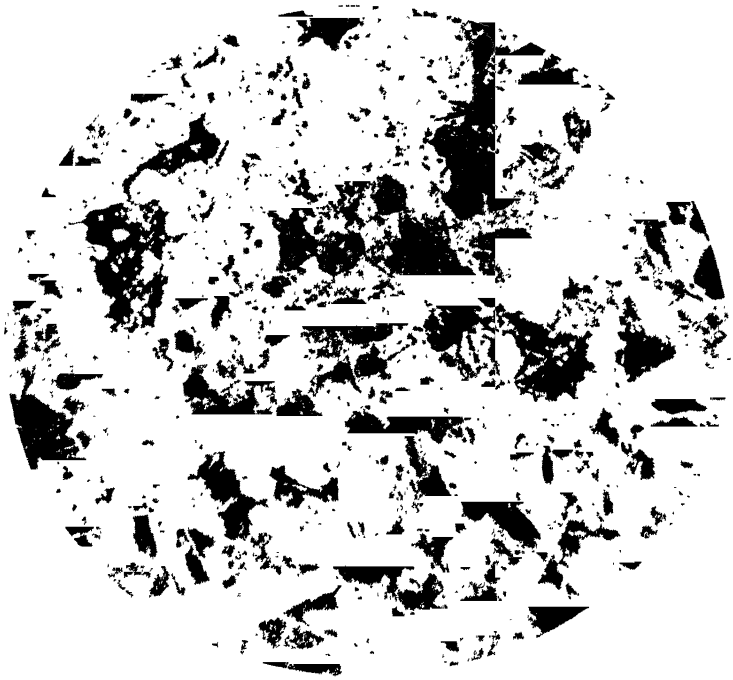


FIG. 36.—NITRIC ACID ETCH. × 400.

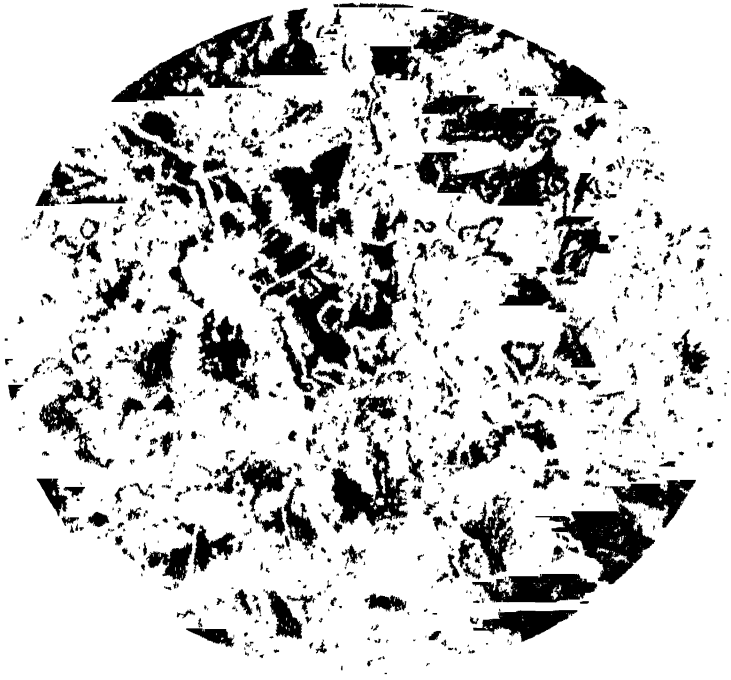


FIG. 37.—SODIUM PICRATE ETCH. × 400.
(Figs. 36 and 37 both reduced 56 per cent., original magnification given.)

FIG. 38.—NITRIC ACID ETCH. × 3500.

FIG 39.—NITRIC ACID ETCH. × 3500.
(Figs. 38 and 39 both reduced 56 per cent., original magnification given)

the austenite, causing the critical point noted by Hadfield and Hopkinson, and has left the carbide isolated in galaxies of small dots. This explanation also tallies with the findings of Dr. Zay Jeffries[7] that manganese steel, after long annealing at 500° C., shows well marked alpha iron lines in an X-ray spectrogram.

Cast 12 per cent. manganese steel, having a coarser structure than the rolled material, shows these characteristic changes more clearly than does the rolled steel, as is shown by Figs. 36 to 40, taken from a bar of cast 12 per cent. manganese steel which has been heated for 48 hr. at

FIG. 40.—NITRIC ACID ETCH. × 3500.
(Reduced 56 per cent., original magnification given.)

500° C. Fig. 36 is a view of this specimen at 400 dia. (reduced to 224), etched with nitric acid, in which the carbide networks and troostitic areas are clearly seen. Fig. 37, at the same magnification, shows the same specimen etched with boiling sodium picrate, which has stained the carbides black, the troostite gray. At 3500 dia. (reduced to 1960), etched with nitric acid, the troostitic areas of this specimen are shown in Fig. 38, where the development of pearlite is quite marked; in Fig. 39, where the pearlite is even better developed, and the rib of carbide that

[7] Edward de Mille Campbell Memorial Lecture, Amer. Soc. for Steel Treating, September 21, 1927.

appears dark at low power in Fig. 36 is shown in its true color as carbide; and finally in Fig. 40, a view of a spot where the breaking down of troostite to pearlite has progressed very far.

As some of these photomicrographs are similar to a number of those shown by Dr. Krivobok in his recent paper before the American Society for Steel Treating,[8] I hope I may be excused for mentioning the fact that the photomicrographs I have shown were taken during 1925 and 1926, and have been withheld from publication until the present time.

Clearly, then, the statement once current that manganese steel can not be transformed by any process of heat treatment no longer has a shred of truth attached to it. Prolonged holding at temperatures below its critical point is shown to have exactly the effect that exceedingly slow cooling would have; that is, it gradually releases the brake, to use Howe's metaphor, that the combined effect of carbon, manganese, and comparatively rapid cooling places upon the natural tendency of the steel to transform, and so allows transformation to take place.

Effect of Transformation on Grain Size of Manganese Steel

When manganese steel is poured at a low temperature, its austenite crystals are comparatively small, but when it is cast very hot it has enormous austenite grains, largely in the form of elongated prisms extending at right angles to the surfaces of the piece. This columnar structure is clearly revealed in the microstructure of the metal, and on the fracture of a bar, broken in the untreated state, is seen as an aggregate of columnar fibers resembling the pulp of an orange. Moreover, the austenite grain size that the metal assumes on cooling from the casting temperature persists after the usual heat treatment. It may be obscured in the fracture of a heat-treated bar but the microscope reveals the true grain size to be what it was before heat treatment. This is what would naturally be expected, for ordinarily the metal in cooling never passes below its critical point, but even when cold is still above the critical range. No change in grain size should be expected to result from heating it again, any more than it would in a piece of cast carbon steel if the initial cooling of the latter were interrupted by placing it in a furnace before it had cooled into the transformation range, and the steel were at once brought to a temperature of say 1000° C. and quenched.

Out of hundreds of photomicrographs that I might select to show this coarsely columnar structure in manganese steel castings poured

[8] V. N. Krivobok: A Study of the Constitution of High Manganese Steels. *Proc.* Amer. Soc. Steel Treating (June, 1928).

very hot, I shall use but one, Fig. 41, showing at 60 dia. the structure of a piece of heat-treated cast manganese steel rail, etched with nitric acid in alcohol. This plate was taken in the laboratory of the Taylor-Wharton Co. many years ago; it illustrates well the coarse structure of the steel when poured hot, and the slip lines described earlier in this paper. Parenthetically, I may remark that in obtaining specimens from castings it was always our custom to cut them only partly free from the casting, and to break them off by bending them back and forth with a hammer. In this way we got a fair idea of the toughness of the steel and at the same time developed slip lines in the austenite crystals that made it easier to bring out the structure by etching.

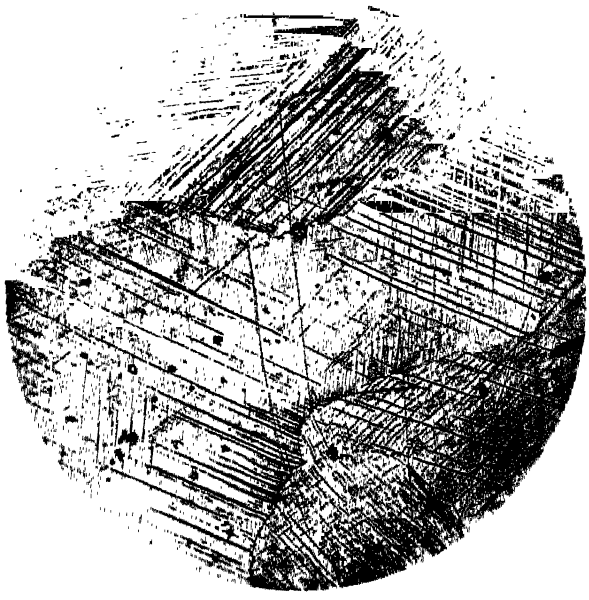


FIG. 41.—NITRIC ACID ETCH. × 60.

In seeking confirmation of our conclusion that the effect of heating manganese steel at 500° C. is a true transformation, we naturally asked ourselves what other effect that transformation is known to have on ordinary steels could be found in 12 per cent. manganese steels. A number of years ago, reasoning from the evidence in Hadfield's and Hopkinson's paper, I came to the conclusion that a change in the austenite grain size should follow a heat treatment consisting of a prolonged annealing at or near 500° C., followed by a second heating to 1060° C. and quenching in water. My thought was that, just as in carbon steel the process of letting the metal transform by slow cooling and then heating it past its transformation point causes a regranulation of the metal, so a similar change in grain size should follow in manganese steel

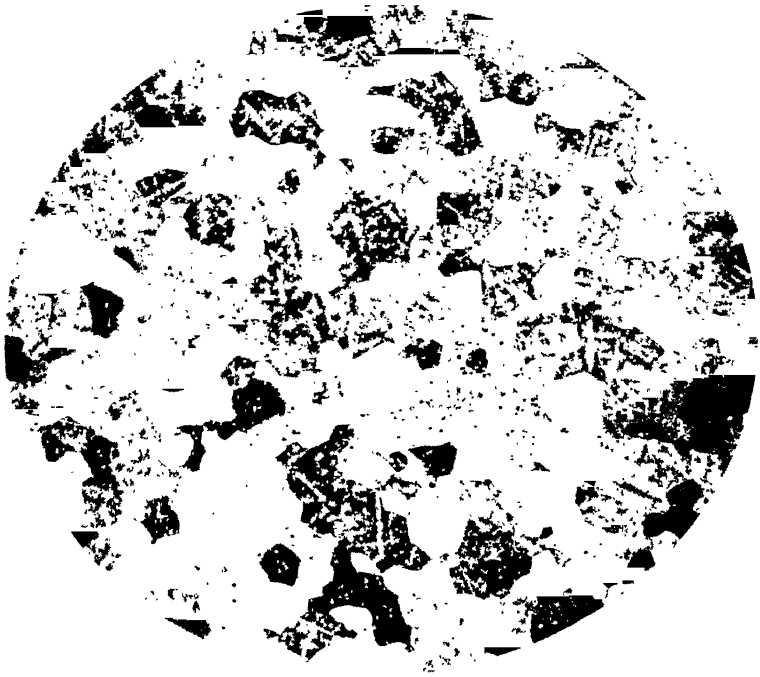


FIG 42.—NITRIC ACID ETCH. × 35.

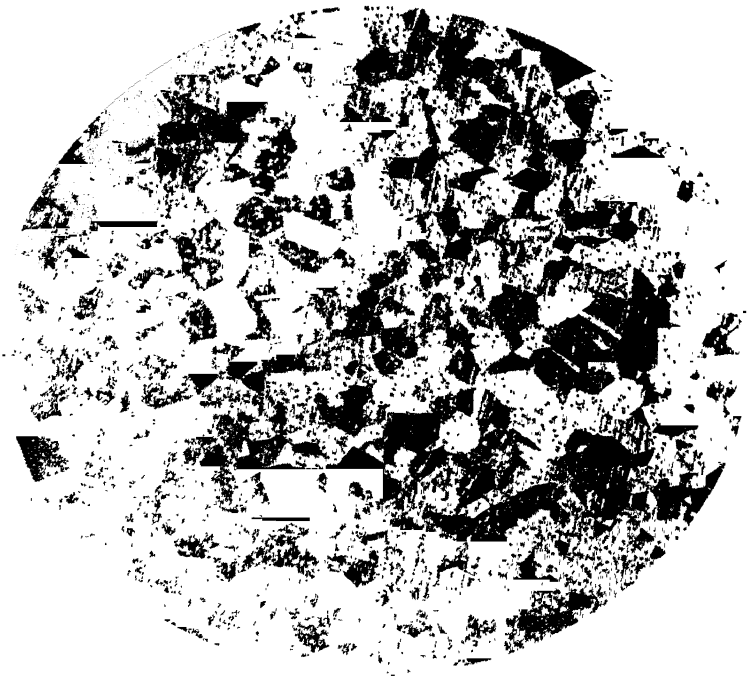


FIG. 43.—NITRIC ACID ETCH. × 35.
(Figs. 42 and 43 both reduced 56 per cent., original magnification given.)

FIG. 44.—NITRIC ACID ETCH. × 35.

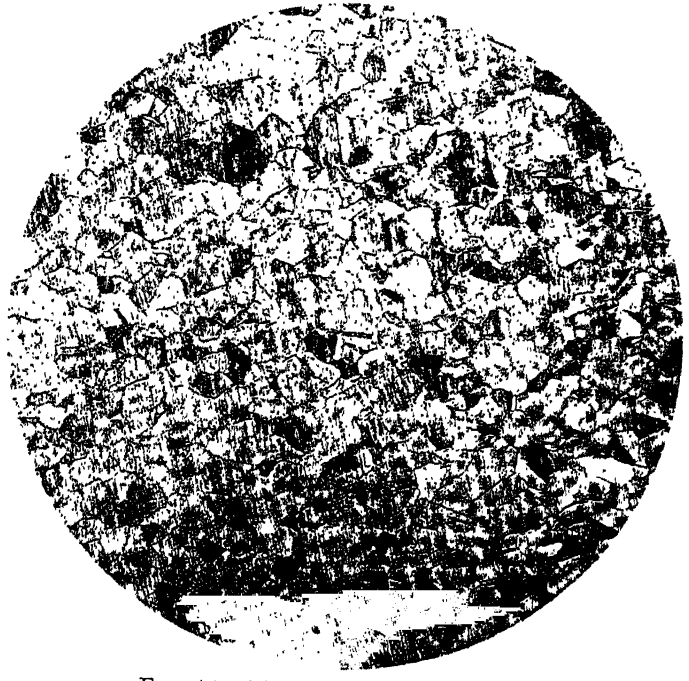


FIG. 45.—NITRIC ACID ETCH. × 35.

(Figs. 44 and 45 both reduced 56 per cent., original magnification given.

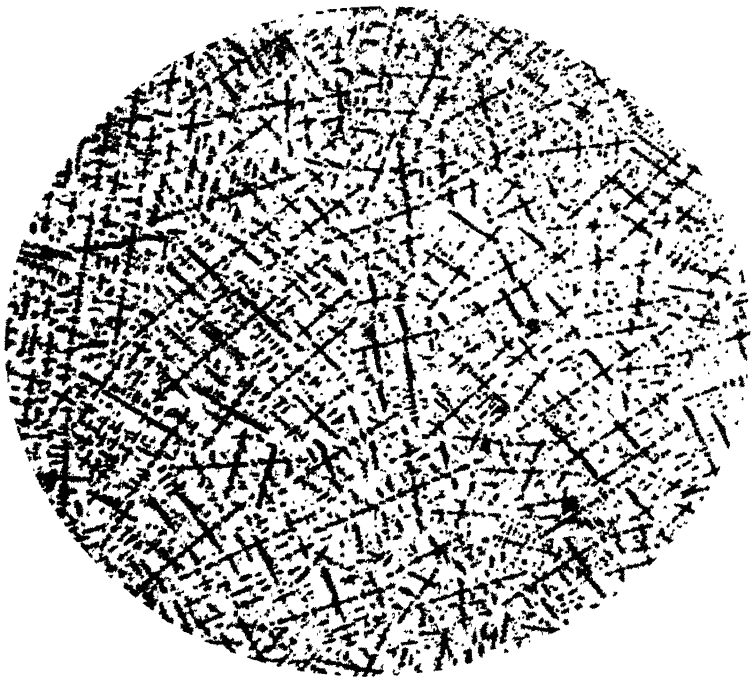


FIG. 46.—SODIUM PICRATE ETCH. × 35.

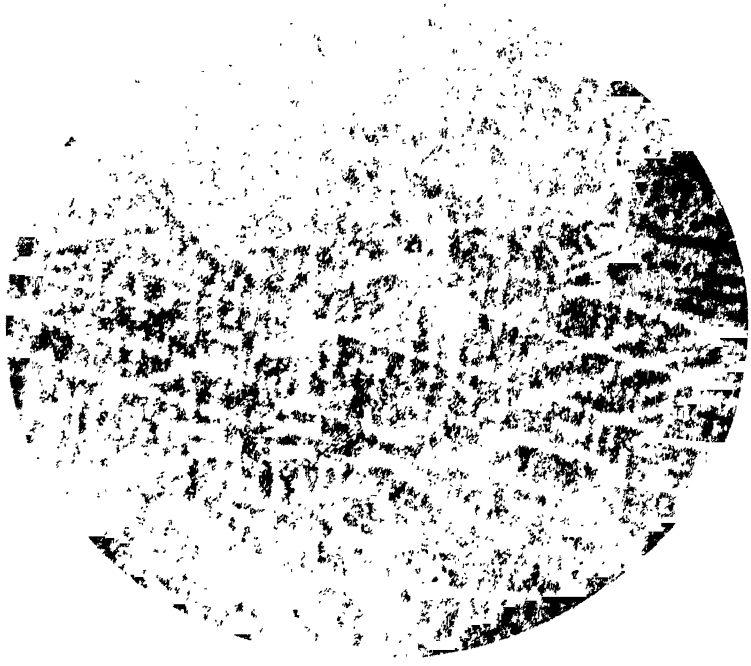


FIG. 47.—SODIUM PICRATE ETCH. × 35.
(Figs. 46 and 47 both reduced 56 per cent., original magnification given.)

if it is transformed by long annealing at a low temperature and then again heated past this critical range. That my reasoning was correct will be shown in the remaining photomicrographs of this paper, which were made from specimens taken from the grip ends of tensile test bars. These bars were made and tested in order to ascertain the effect of the anticipated change in grain size upon the physical properties of the steel. They were cast in pairs on coupons provided with liberal sink-heads, as shown in Fig. 56, were cut from the coupons with a thin abrasive wheel before being heat-treated, and were ground after heat treatment to the dimensions shown in Fig. 57.

Figs. 42 to 53 inclusive were magnified 35 dia. (reduced to 19), while the magnification of Figs. 54 and 55 was 4.3 dia. Figs. 42 to 47 are from a heat of cast manganese steel analyzing carbon 1.22 per cent., silicon 0.73 per cent., manganese 11.5 per cent.

Fig. 42 shows a test bar cast "cold," etched with nitric acid, which has been heat-treated simply by heating it to 1060° C. and quenching it in water. The grain count is 22 grains per square millimeter. The companion bar from the same coupon, heat-treated by annealing for 48 hr. at 500° C., cooling in air, then heating to 1060° C., and quenching in water, is shown in Fig. 43, also etched with nitric acid. The grain count is 46 grains per square millimeter.

Fig. 44 shows the structure with nitric acid etch of a bar from another coupon of the same heat, cast very hot, which has been heated to 1060° C. and quenched in water. The grain count is 9 per square millimeter. The companion bar from the same coupon, similarly etched, is shown in Fig. 45, after annealing 48 hr. at 500° C. and cooling in air, followed by heating to 1060° C. and quenching in water. The grain count is 48 grains per square millimeter.

At the same magnification, but etched with boiling sodium picrate, the specimens from the hot-poured bars are shown in Fig. 46, taken from the piece heated to 1060° C. and quenched in water, and in Fig. 47, from the bar annealed 48 hr. at 500° C. and air-cooled, followed by heating to 1060° C. and quenching in water. The dendritic structure, so marked in Fig. 46, appears to have been partly obliterated in the steel annealed at a low temperature before the usual heat treatment.

Figs. 48 to 55 are from specimens of cast manganese steel, containing carbon 1.16 per cent., manganese 12.9 per cent., silicon 0.54 per cent., phosphorus 0.079 per cent.

Fig. 48, etched with nitric acid, shows the structure of a bar cast "cold," heated to 1060° C. and quenched in water, with a grain count of 47 grains to the square millimeter, and Fig. 49, the companion bar from the same coupon, similarly etched, after annealing 48 hr. at 500° C. and cooling in the air, followed by heating to 1060° C. and quenching in water. The grain count is 76 grains per square millimeter. Fig. 50

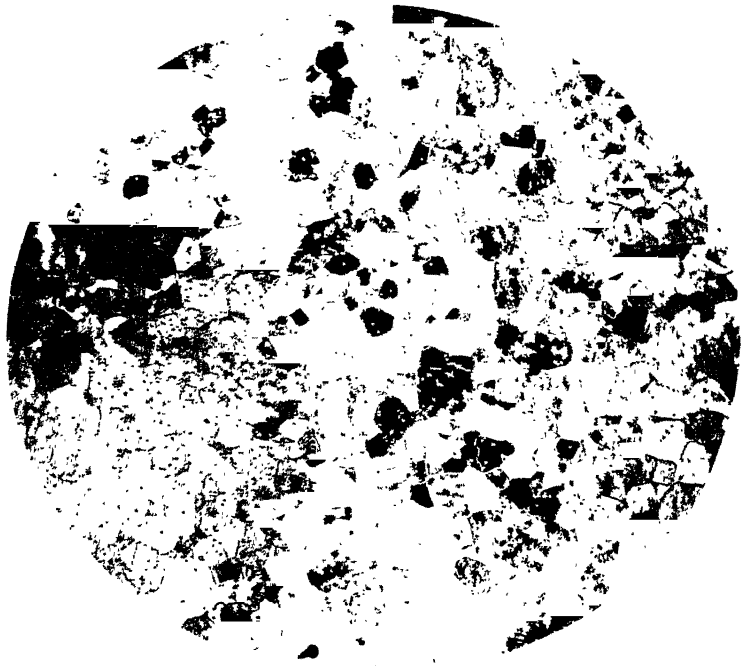


FIG. 48.—NITRIC ACID ETCH. × 35.

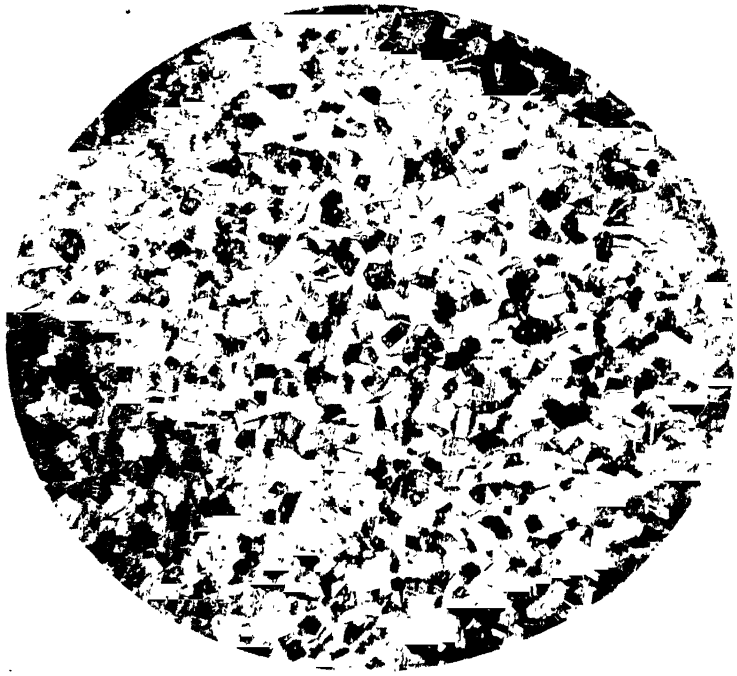


FIG. 49.—NITRIC ACID ETCH. × 35.
(Figs. 48 and 49 both reduced 56 per cent., original magnification given.)

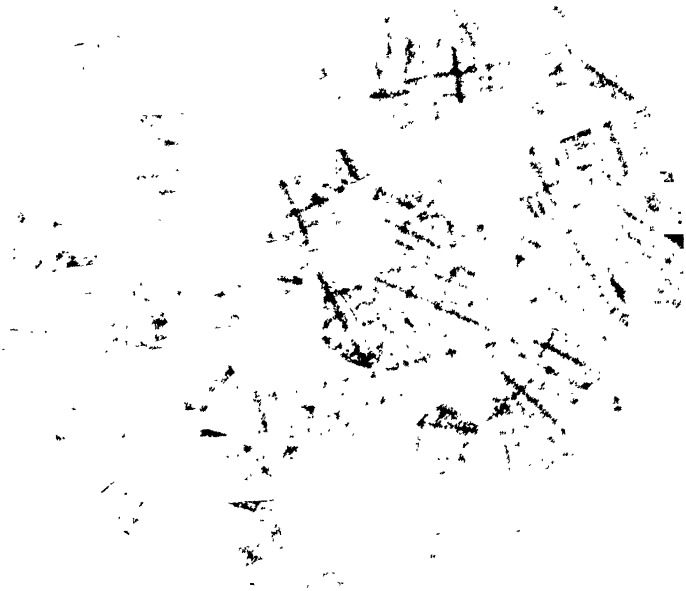


FIG. 50.—NITRIC ACID ETCH. × 35.

FIG. 51.—NITRIC ACID ETCH. × 35.
(Figs. 50 and 51 both reduced 56 per cent., original magnification given.)

FIG. 52.—SODIUM PICRATE ETCH. × 35.

FIG. 53.—SODIUM PICRATE ETCH. × 35.
(Figs. 52 and 53 both reduced 56 per cent., original magnification given.)

shows a bar cast hot, etched with nitric acid, which has been simply heated to 1060° C. and quenched in water, the grain count being 6 to the square millimeter in spots, and 67 to the square millimeter in other places. After the double heat treatment, the companion bar from the same coupon is shown in Fig. 51. The grain count in this specimen is 90 grains per square millimeter. Both specimens show traces of dendritic structure.

FIG. 54.—NITRIC ACID ETCH. × 4.3.

Etched with boiling sodium picrate the hot-poured specimens, shown in Figs. 50 and 51, exhibit the marked dendritic structures of Fig. 52, which is taken from the bar given the single heating, and of Fig. 53, from the bar annealed at 500° C. and cooled in air, then heated to 1060° C. and quenched in water. In this case it is evident that the double heat treatment has not been effective in eliminating dendritic structure, as it

FIG. 55.—NITRIC ACID ETCH. × 4.3.

was in the specimens shown in Figs. 46 and 47. We are uncertain, therefore, whether or not the double heat treatment tends to lessen dendritic segregation.

Finally, Fig. 54 shows the entire area of the hot-poured specimen of Figs. 50 and 52, etched with nitric acid and magnified 4.3 dia. The coarse grains of the steel are plainly evident. Fig. 55, similarly etched

and at the same magnification, shows the structure of the companion bar that was annealed at 500° C. for 48 hr. and cooled in air, then heated to 1060° C. and quenched in water. The change in average grain size brought about by the double heat treatment is most striking.

In addition to the change in grain size, the double heat treatment appeared to affect to some extent the number and arrangement of the white threads in the austenite of the specimens, such as were shown in the

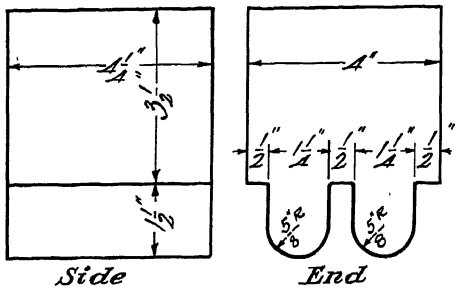


FIG. 56.—COUPON.

earlier parts of this paper. The evidence on this point, however, is far from clear.

The effect of the changes in grain size produced by the double heat treatment upon the tensile properties of the steel is shown in Table 1, in which the companion bars from each coupon are shown consecutively. The symbols "C" and "H" represent "cold-poured" and "hot-poured" steel, heated to 1060° C. and quenched in water; "Cr" and "Hr" denote

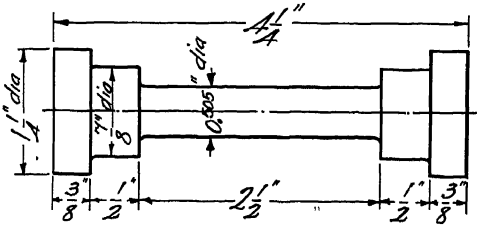


FIG. 57.—TENSILE TEST BAR.

the companion bars that were given the double heat treatment. In a number of cases the limit of proportionality in tension was determined with an Olsen strain gage type of extensometer reading to 0.00006667 in. This property varied so little, however, that it was not thought worth while to determine it in all our tests.

It will be seen that in practically every case the tensile strength, elongation, and reduction of area of the steel have been improved by the double heat treatment, the improvement being more marked in the metal poured hot, which is generally weaker and less ductile than the

cold-poured steel. Test Hr on heat B indicates that the strongly marked dendrites shown in that specimen, as illustrated in Figs. 51 and 53, have but little harmful effect on the properties of the steel.

TABLE 1.—*Effect on Tensile Properties of Manganese Steel of Changes in Grain Size Produced by Double Heat Treatment*

Heat	C	Si	P	Mn	State	Tensile Strength	Proportional Limit	Elong. in 2 In., Per Cent.	Red. of Area, Per Cent.	Grains per Sq. Mm.	Fig. No.
A	1.22	0.73	0.085	11.5	C	95,750	42,500	27.0	35.4	22	42
					Cr.	130,000	45,000	43.5	31.2[a]	46	43
					H	78,000	37,500	17.8	27.9[b]	9	44–46
					Hr.	97,500	42,500	19.75	34.4[b]	48	45–47
B	1.16	0.54	0.079	12.9	C	134,750	42,500	54.35	42.5	47	48
					Cr.	148,000	45,000	60.4	45.7	76	49
					H					6–67	50–52–54
					Hr.	147,750	45,000	62.0	44.9	90	51–53–55
C	1.17	0.72		13.6	H	126,000	43,750	59.2	45.4		
					Hr.	143,000	42,500	71.2	46.3		
D	1.13	0.78		13.6	C	130,500	45,000	52.0	37.9		
					Cr.	136,000	45,000	66.7	44.3		
E	1.29	0.74		13.7	C	115,750	45,000	40.4	33.4		
					Cr.	146,000	47,500	55.8	40.7		
					H	120,000		50.5	41.6		
F	1.17	0.77		13.9	C	140,000		50.9	41.3		
					C	128,500		46.7	40.3		
G	1.18	0.76		13.3	C	136,750		53.0	41.0		
					C	132,500		50.25	47.2		
H	1.24	0.84	0.086	13.0	C	133,250	46,250	47.4	45.1		
					Cr.	148,250	47,500	52.4	37.6[a]		
					H	112,000	41,250	47.0	33.1		
					Hr.	152,750	48,750	63.6	44.3		
I	1.27	0.63		12.5	C	101,000		28.3	38.8[b]		
					Cr.	137,500		48.8	43.1		
					H	98,500		37.0	34.7		
					Hr.	125,500		37.8	34.1[ab]		

[a] Broke outside marks. [b] Slight flaw.

In Table 2 are given the average tensile strengths and extensions of the different classes of tests in Table 1. In this table we see at a glance the considerable improvement in these properties caused by the double heat treatment.

In tensile bars cast roughly to shape, and in most small castings, improvements in the tensile properties, comparable in amount to those illustrated in these tables, are not produced by the double heat treat-

TABLE 2.—*Summary of Tests in Table* 1

State	No. Tests	Tensile Strength	Elong. in 2 In., Per Cent.
C	10	124,875	45.03
Cr.	6	140,960	54.6
H	5	106,900	42.3
Hr.	5	133,300	50.87

ment. The reason for this is not entirely clear, though it appears to be due in part to the fact that the centers of these bars contain an area of spongy metal, which is considerably more extensive in the bars poured hot than in those poured cold, and is sufficiently large to mask the effect of improvement in the strength of the outside portion of the bars. Our experiments in applying this treatment to heavier castings, too, led to negative results, and were not pushed very far for the obvious reason that heavy castings are almost invariably poured cold and therefore require little improvement in their tensile properties.

TABLE 3.—*Repeated Bending Tests*

Size of Bar, Inches	Throw, Inches	State	No. Tests	Revolutions to Break
¾ round	⅜	H	20	13,800
¾ round	⅜	C	15	20,325
¾ round	⅜	Hr.	9	22,600
¾ square	¼	H	10	14,663
¾ square	¼	Hr.	11	25,212

That the double heat treatment improves certain properties of bars cast to size, however, is shown by the results of repeated bending tests summarized in Table 3. These tests were made in an Olsen machine in which ¾-in. round or square bars are clamped tightly at one end, while the free end is moved back and forth by a cross-head 6½ in. from the vise that holds the bar. The "throw" shown in the table is the total motion of the end of the bar from its lowest to its highest position, and is probably sufficient to give the bar a very slight permanent set. The hot-poured bars H, which have been given the ordinary heat treatment, break after about one-half the number of bends that are endured by the heat-treated cold-poured bars C or by the hot-poured bars Hr that have received the double heat treatment.

In these tests, of course, the determining factor is the strength of the outside fibers, for when a crack starts on the outside of a bar, the latter breaks after only a few hundred more bends. The effect of sponginess at the center, therefore, which appears to affect the result

of tensile tests of bars cast to size, is practically nil in bars subjected to repeated small bends, so that the number of bends they endure in this test is roughly proportional to the strength of the metal of the outside layers.

In going over our recent work on manganese steel to select the material for this paper, I have been impressed, not by what we have learned, but by what we have still to find out. It is no exaggeration to say that we have only made a start, and that for one fact we have established there remain hundreds still to be ascertained. Nothing could give greater satisfaction to Henry M. Howe, could he still be here with us, than to see, as so many of us shall see, the steady expansion of our knowledge of this and other steels by the labors of the many earnest investigators now at work in the field where he labored so long, so faithfully, and so successfully.

Gases Extracted from Iron-carbon Alloys by Vacuum Melting

By N. A. Ziegler,* East Pittsburgh, Pa.

(New York Meeting, February, 1929)

The present publication is a continuation of the work on gas analysis, described in a paper presented before the Institute of Metals Division a year ago.[1] While that paper was largely descriptive in character, dealing with the various parts of the apparatus and method of operations, the present one gives numerical data obtained as a result of a series of experiments with iron-carbon alloys. The apparatus and the methods applied are essentially the same as previously described, changes being only in minor details.

Attention should be called to the fact that in the present work we are dealing with the gaseous mixtures obtained as a result of vacuum melting of various ferrous alloys. It should be understood that when the terms "degasified sample" and "products of degasification" are used, they refer to the sample remaining after the vacuum fusion of the alloy and the gaseous products removed therefrom, respectively. The writer does not wish to create the impression that the metallic products of this process are absolutely free from any gaseous elements, nor that the gases obtained are present as such in the original sample. These two points are not yet definitely known and are subjects for future investigation.

The point, however, which has been established beyond doubt, is that all the gases dealt with come from the metallic charge and are present either in the charge as such, or are produced as a result of chemical reactions going on within the charge. The suggestion that the gases are due to the reactions between the metallic charge and the refractory materials has no valid basis.

General Procedure

A series of iron-carbon alloys was prepared in a magnesia-lined graphite crucible placed in a high frequency laboratory furnace open to the atmosphere. The materials used were Westinghouse electrolytic iron and Acheson graphite. Each alloy, after it was completely molten, was kept in the liquid state for 10 min., cast into a small iron mold, and

* Research Laboratory, Westinghouse Electric & Manufacturing Co.

[1] P. H. Brace and N. A. Ziegler: Application of High-vacuum Induction Furnace to the Study of Gases in Metals. *Proc.* Inst. of Metals Div. (1928) 544.

cooled in air to room temperature. In this way, a series of castings, weighing about 1 kg. each and ranging in carbon content from 0.0038 to 4.45 per cent., was obtained (Table 1). In preparing these samples,

TABLE 1.—*Laboratory-prepared Castings Used in Gas Analysis Experiments*

Sample No.	I'-1	I'-2	I'-3	I'-4	I'-5	I'-6	I'-7	I'-8	I'-9	I'-10	I'-11	I'-12	I'-13	I'-14	I'-15	I'-16	I'-17	I'-18	I'-19	I'-20
Run No.	183	184	185	186	187	188	189	190	194	195	196	237	239	240	245	250	252	253	255	254
Nature of the Sample	Laboratory Iron-Carbon Alloys											Frey Cast Iron	Gas Engine Piston	Nails	Pittsburgh Steel Co.					
															Billet Steel Rods	Billet Steel Rods	¾" Wire			
															Open Hearth	Crucible	Open Hearth	Crucible	Crucible	Crucible
															Annealed	Annealed	Annealed	Annealed	Annealed	Annealed
(1) Carbon added or assumed	0	.01	.06	.08	.10	.30	.50	1.00	2.00	4.00	6.00	3.60 to 3.25	?	?	.13	.13	.10–.14	.10–.14	95 and under	95 and under
H_2O																				
(2) % by weight of the sample	.00118	.00018	.00022	.00016	.00643	—	.00012	—	—	—	—	—	—	—	.00010	.00022	.00081	.00091	.00072	.00106
(3) % by weight of the total gas	4.5	.9	.8	.4	1.1	—	.1	—	—	—	—	—	—	—	—	.1	.2	.2	1.0	1.3
(4) % by volume of the sample	11.3	1.7	2.1	1.6	4.1	—	1.1	—	—	—	—	—	—	—	1.0	2.0	7.8	8.6	6.9	10.1
(5) % by volume of the total gas	4.5	1.5	1.3	.5	2.0	—	.2	—	—	—	—	—	—	—	—	.1	.4	.3	1.8	2.2
CO_2																				
(6) % by weight of the sample	.00770	.08400	.06606	.01083	.01400	.01063	.01760	.03110	.07432	.07000	.04532	.04813	.03900	.01268	.05710	.03440	.06582	.07092	.03225	.02631
(7) % by weight of the total gas	28.9	20.9	21.8	25.8	36.3	27.7	14.9	8.0	3.6	9.1	4.2	2.2	4.1	2.9.2	20.7	12.7	18.2	17.4	47.3	33.0
(8) % by volume of the sample	29.8	15.7	24.7	42.3	59.5	41.6	68.3	121.9	289.6	281.0	185.2	70.8	93.2	49.3	56.0.0	138.0	243.1	276.3	138.2	102.3
(9) % by volume of the total gas	12.0	13.8	15.5	13.8	26.2	19.6	9.8	5.2	6.0	6.2	2.8	1.4	2.6	16.5	27.0	7.4	12.7	10.9	35.6	22.6
CO																				
(10) % by weight of the sample	.01012	.00800	.01631	.02770	.02100	.02425	.09630	.35620	.67900	.68200	.01390	.79500	.55000	.02835	.21700	.22410	.28650	.27904	.03239	.03865
(11) % by weight of the total gas	40.4	47.1	58.8	65.9	54.4	63.2	81.5	90.2	88.2	88.8	94.5	95.2	94.1	65.3	78.5	82.5	79.3	69.1	47.5	48.4
(12) % by volume of the sample	66.2	55.4	100.0	242.5	129.2	149.5	592.0	2162.0	4175.0	4175.0	6241.3	4890.0	3390.5	174.5	3350	1381.0	1765.1	1723.0	193.2	2625
(13) % by volume of the total gas	26.7	48.4	62.7	79.4	62.1	70.1	85.1	92.9	87.2	91.7	95.9	95.9	95.5	58.5	64.6	73.6	81.8	68.2	51.4	55.9
O_2																				
(14) % by weight of the sample	—	.00030	.00019	.00077	[illegible]	.00032	.00120	.00064	.00068	.00115	—	.00121	—	.00021	.00123	.00259	.00165	.00368	.00107	.00073
(15) % by weight of the total gas	—	.16	.7	1.8	1	.8	.2	.1	—	.2	—	.1	—	.5	.4	1.0	.5	.9	1.6	.9
(16) % by volume of the sample	—	1.6	1.0	4.2	[illegible]	1.8	1.1	3.4	2.6	6.2	—	6.6	—	1.1	6.4	14.0	8.9	19.9	5.8	3.9
(17) % by volume of the total gas	—	1.4	.6	1.4	5	.8	.2	.1	—	.1	—	.1	—	.4	.3	.8	.5	.7	1.5	.9
H_2																				
(18) % by weight of the sample	.00122	—	—	—	—	—	.00010	—	.0026	—	—	—	—	—	.00075	.00019	.00332	.00072	.00338	.00032
(19) % by weight of the total gas	4.6	—	—	—	—	—	.1	—	.3	—	—	—	—	—	1.7	.1	.1	.2	.8	.5
(20) % by volume of the sample	104.2	—	—	—	—	—	8.3	—	224.1	—	—	—	—	—	64.1	163.2	277.3	61.6	204.0	28.4
(21) % by volume of the total gas	41.5	—	—	—	—	—	1.2	—	4.7	—	—	—	—	—	21.5	7.9	14.8	2.9	8.1	7.3
N_2																				
(22) % by weight of the sample	.00579	.00567	.00496	.00256	.00317	.00317	.00384	.00652	.01497	.01443	.01433	.02105	.01060	.00142	.00080	.00568	.00577	.04638	.00148	.01303
(23) % by weight of the total gas	21.6	29.5	17.9	6.1	8.2	8.3	3.2	1.7	1.3	1.9	1.3	2.5	1.8	3.3	.3	3.6	1.6	11.6	2.1	16.4
(24) % by volume of the sample	36.9	39.5	31.7	14.9	20.2	20.3	24.5	41.6	98.1	92.3	91.6	134.4	67.6	9.1	5.1	61.8	37.0	299.5	9.3	65.1
(25) % by volume of the total gas	14.9	34.7	19.9	4.9	9.7	9.5	3.5	1.8	2.1	2.0	1.4	2.6	1.9	3.1	.2	3.3	1.7	11.8	2.4	18.4
Totals																				
(26) % by weight of the sample	.02661	.01912	.02774	.04202	.03864	.03837	.11816	.35936	.77158	.76758	.07355	.83539	.58450	.04341	.27642	.27131	.31127	.40481	.06823	.07578
(27) % by weight of the total gas	77.4	113.9	158.5	90.5	108.0	213.1	699.3	2328.9	4789.4	4554.5	6518.1	5101.8	3541.3	298.1	2610.7	1874.1	2153.5	2531.3	387.8	451.9
O_2 - % (By Weight) of total gas																				
(28)	48.1	44.5	50.9	58.6	58.5	57.1	57.7	57.5	57.4	57.5	57.1	56.1	56.8	55.1	60.4	57.4	59.3	53.3	64.0	59.7
O_2 - % (By Weight) of the sample																				
(29)	.01244	.00851	.01414	.02463	.02256	.02193	.06821	.22706	.44279	.44205	.61189	.46839	.34255	.02565	.16692	.15590	.21769	.21621	.04364	.03525
C - % (By Weight) of total gas																				
(30)	25.2	25.9	29.2	35.2	33.2	34.7	39.0	40.9	40.4	40.6	41.6	41.4	41.4	35.0	32.4	39.0	38.9	34.4	34.3	29.7
C - % (By Weight) of the sample																				
(31)	.00669	.00495	.00864	.01484	.01282	.01328	.04610	.16281	.31301	.31109	.44687	.34268	.24643	.01559	.10865	.10539	.14066	.13892	.02246	.02373
C - % By direct chemical analysis of the original sample																				
(32)	.06584	.00377	.00744	[illegible]											.05761	.08693	.07161	.07386	.04534	.01275	.01245
C - % By direct chemical analysis of the vacuum treated sample																				
(33)	.0013	—	.00072	.00465	.00087	.00109	—	.13	.14	.00245	3.25	4.40	2.20	2.96	.02083	.00332	.00263	.00423	.00263	—	—
C - % (By Weight) of sample lost in preparation of samples (1) - (32)																				
(34)	.00584	.00623	.05756	.07138	.09282	.78970	.47089	.72539	.87455	.75	1.55									
O_2 - % (By Weight) of sample corresponding to carbon lost in preparation of samples (34)																				
(35)	.00779	.0083	.07010	.09510	.12380	.39050	.62750	.54750	.46800	.00100	2.8500									
O_2 - % (By Weight) of sample corresponding to carbon retained in the original sample. (32)																				
(36)	.00779	.00543	.00993	.01149	.00957	.01374	.03880	.3648	1.5000	4.34	5.87									
O_2 - % (By Weight) of sample corresponding to carbon retained in vacuum treated sample (33)																				
(37)	.00175	—	.00029	.00087	.00116	.00145	—	.17530	.33400	.43000	5.86000									
O_2 - % (By Weight) of sample corresponding to carbon added (1)																				
(38)	0	.01532	.08000	.10680	.1332	.4000	1.6670	1.3320	2.6620	5.8300	8.4000									

difficulty was experienced with only one alloy (I'-11) to which such a large amount of graphite was added that it took a considerable time (about ½ hr.) to get it all dissolved in the iron. Once the carbon was completely dissolved, this alloy was also kept in molten state for 10 min.

and then cast in a way similar to the rest. Chemical analysis (see Table 1, item 34 and Fig. 7, item 34) shows that a considerable part of the carbon added is oxidized during preparation of the alloys. The carbon content of each alloy is shown in Table 1, item 32. Only alloy I′-11, which looked like spiegeleisen, showed free graphite to the naked eye.

Each of these alloys was remelted in the bell jar vacuum furnace, the gases given off being collected and analyzed in the way described in the previous paper.[2] High refractory porcelain crucibles were used for remelting the alloys, and the "refractory correction" was applied in each case in the ordinary way.

All alloys before vacuum treatment are distinguished by the symbol I′; the same alloys after the vacuum treatment are distinguished by the symbol I'_1.

It is interesting to note that in the case of low-carbon alloys, *i. e.*, I′-1 to I′-7 containing up to 0.0291 per cent. C, a moderate amount of gases was obtained, and no difficulties were experienced in degasifying the samples, while for the high-carbon samples, and especially for I′-11, the amount of gases that could be extracted was so great that it took sometimes two days to degasify the sample completely. But in all cases, for low-carbon as well as for high-carbon samples, a very definite end point in the vacuum melting was observed. The sample was kept in the molten state and the gases produced continuously removed until the furnace vacuum fell to a value of about 0.001 mm. Hg. In every case there was a very marked and rather sudden improvement in the furnace vacuum, always coincident with the formation of a heavy black deposit on the inside of the bell jar. This point is emphasized because it meets the objection made by some that most of the gases determined by our method are the products of the chemical reaction of carbon in the sample and oxygen in the refractories. If this were the case, the evolution of gases would proceed until complete decarburization of the sample, or complete deoxidation of the refractory had taken place. But such is not the case. Complete degasification of the sample, manifested, as stated before, by a sudden improvement in the furnace vacuum and the formation of a black deposit in the bell jar, occurs when the chemical analysis of the degasified sample shows sometimes as high as over 4.00 per cent. C (I'_1-11), and the walls of the crucible are scarcely corroded at all.

As a further check on this important point, the following two experiments were performed:

1. Part of a degasified sample (I'_1-11) was placed in the bell jar furnace, and, after pretreatment in the regular way, was melted and the gases collected and analyzed. The total amount of the gases obtained

[2] P. H. Brace and N. A. Ziegler: *Loc. cit.*

was extremely small as compared with that obtained as a result of the first degasification of the same sample, being of the same order as the "blank correction" for the refractories.

2. It has been found by a series of experiments, not described in the present paper, that the maximum amount of oxygen which can be extracted from the Niagara Falls Electrolytic Iron Co.'s electrolytic iron, by adding to it various amounts of carbon as deoxidizer, and by degasifying in the bell jar furnace, is 0.448 per cent. by weight.

An empty graphite crucible was degasified in the bell jar furnace by heating it to a white heat. The evolution of the gases by the graphite was tremendous, and it took a very long time to obtain a vacuum of 0.08 mm. Hg in the furnace. This was the best vacuum that could be obtained with the crucible at a white heat, whereas a final pressure of about 0.001 mm. Hg is ordinarily obtained at the conclusion of an experiment. After cooling the crucible down to room temperature in vacuum, it was kept in air at room temperature for 24 hr. when it was again vacuum-treated. This time the final pressure obtained was 0.04 mm. Hg. All the gases were collected and analyzed, and the results used as a "blank correction" for melts made in the graphite crucible. This correction is about 14 times higher than the correction established and applied for the porcelain crucibles, being 27.9 per cent. of the total gas obtained from electrolytic iron, while the corresponding correction for the porcelain crucible is only 2.3 per cent. A charge of the Niagara Falls electrolytic iron was introduced in the degasified crucible, and melted in the bell jar furnace. The gaseous products of the run were collected and analyzed. The finishing furnace vacuum was 0.03 mm. Hg (the best vacuum that could be obtained). The total oxygen obtained in this way was 0.514 per cent. by weight. Considering the much greater possible error in this case than when a porcelain crucible is used, this is a very satisfactory check (0.514 vs. 0.448 per cent.), and leaves very little doubt as to the suitability of the porcelain crucibles for the vacuum melting.

Water vapor has been found in the low-carbon samples only (Table 1, items 2, 3, 4 and 5). The significance of this fact is not yet fully understood. It is possible that H_2 in high-carbon samples combines with C, is eliminated as hydrocarbon gas, and is analyzed as CO_2.

Carbon dioxide is found in all samples, its amount increasing with the increase of carbon. Only in I'-11, containing free graphite, the amount of carbon dioxide is unusually low. (See Table 1, items 6, 7, 8 and 9, and Figs. 1 and 2, curves 6 and 8.)

Carbon monoxide is the principal constituent of the gaseous mixture in all cases. In the case of very low carbon alloys the amount increases but slightly with increase of carbon. But when the carbon content exceeds about 0.01 per cent., the amount of carbon monoxide increases

very rapidly up to about 1 per cent. C, and with further increase of carbon remains constant at about 44 times the volume of the sample, computed on the basis of normal temperature and pressure. However, when the carbon content of the original sample exceeds 4 per cent., with

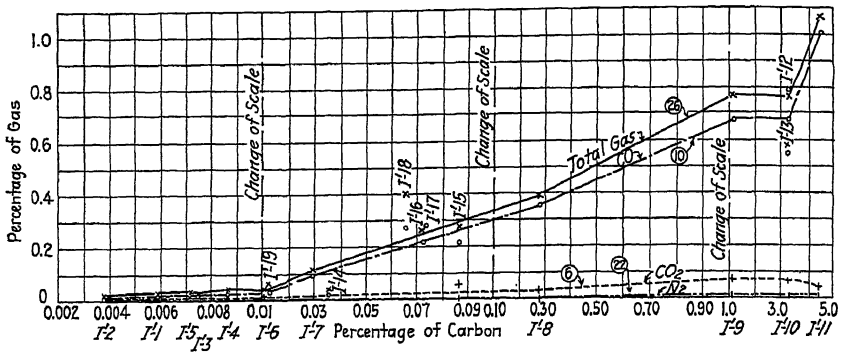


FIG. 1.—GAS PERCENTAGE (BY WEIGHT) OF SAMPLE VS. CARBON CONTENT.

free graphite present, the amount of carbon monoxide extracted is over 60 times the volume of the original sample at normal temperature and pressure. (See Table 1, items 10, 11, 12, 13 and Figs. 1 and 2, curves 10 and 12.)

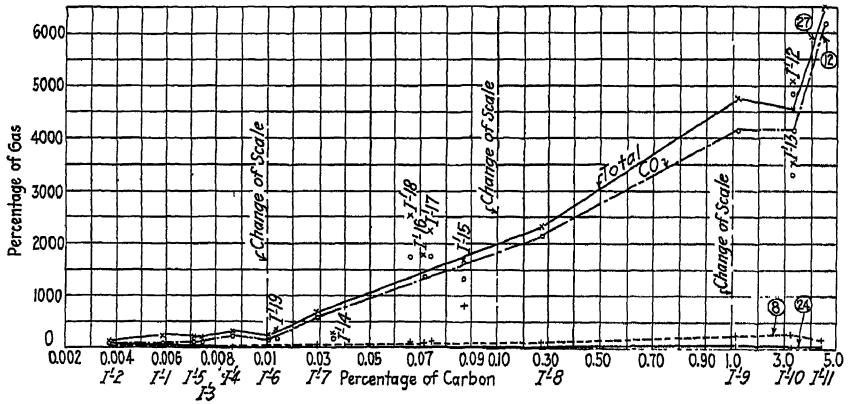


FIG. 2.—GAS PERCENTAGE (BY VOLUME) OF SAMPLE VS. CARBON CONTENT.

Free oxygen has been found present in nearly all the samples but in negligible quantities (Table 1, items 14, 15, 16, 17).

Traces of hydrogen were found in three alloys (Table 1, items 18, 19, 20, 21) and may be due to experimental errors, so that it is safe to state that the laboratory samples contain no appreciable amount of free hydrogen.

Small and varying amounts of nitrogen are present in the samples, probably due to occluded air (Table 1, items 22, 23, 24, 25 and Figs. 1 and 2, curves 22 and 24).

Since the principal constituent of the extracted gases is carbon monoxide, its amount plotted against the carbon content of the original sample gives a curve of the same general shape as the curve of the total gas content (Table 1, Figs. 1 and 2, items and curves 10, 12, 26, 27).

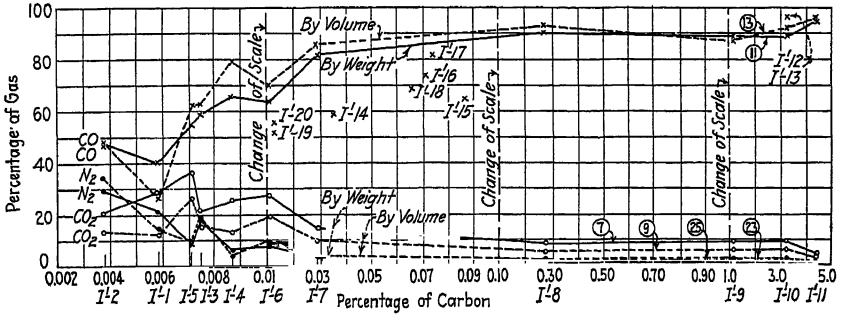


FIG. 3.—GAS PERCENTAGE BY WEIGHT AND VOLUME OF THE TOTAL GAS VS. CARBON CONTENT.

The above results, computed as percentages of the total gaseous mixture, are shown in Fig. 3, curves 7, 9, 11, 13, 23, 25. For carbon above 0.03 per cent., CO is predominating in the gaseous mixture and the curves consequently become horizontal for increasing carbon contents.

DISCUSSION OF THE RESULTS

From the values of carbon dioxide and monoxide, and from the small amounts of free oxygen and water vapor, the total amounts of

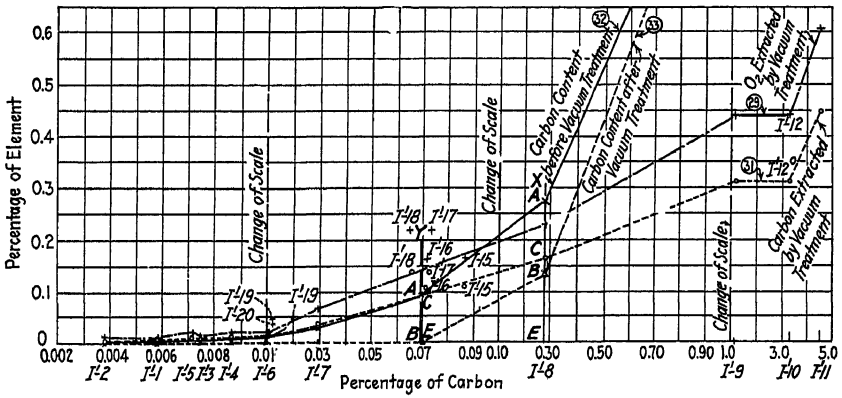


FIG. 4.—ELEMENT PERCENTAGE (BY WEIGHT) OF SAMPLE VS. CARBON CONTENT.

oxygen and carbon extracted by vacuum treatment have been computed for each sample. (Table 1, items 29 and 31.) In Fig. 4 the following

curves have been plotted, using the carbon content of the original sample as abscissa:

Curve 32.—Carbon content of the original sample (45° straight line, if the abscissa and the ordinate are given to the same scale).

Curve 33.—Carbon content of the samples after the vacuum treatment.

Curve 31.—Carbon extracted from the sample during degasification, in form of carbon dioxide and monoxide.

Curve 29.—Oxygen extracted from the samples during degasification, in form of different gases.

It will be seen that curve 33 coincides with the abscissa for $C < 0.07$ per cent., *i. e.* the samples after the vacuum treatment come out practically decarburized, and only for $C > 0.07$ per cent. which may be called the "critical" carbon content does the curve begin to ascend. This indicates that the original samples did not contain enough oxygen to eliminate completely more than about 0.07 per cent carbon. Curves 31 and 32 should theoretically coincide up to the critical carbon content, after which curve 32 should have a sharp bend upwards, while curve 31 should remain constant. What actually takes place is that curve 31 continues to ascend but at a smaller slope than curve 32, indicating that for some as yet unknown reason the amount of oxygen absorbed by the iron-carbon alloys, during the process of preparation, becomes greater with increase in the amount of carbon added. The explanation will probably be found when the ternary diagram of iron-oxygen-carbon is definitely established.

The following observations may be made in connection with Fig. 4:

1. Below the "critical" carbon content at which point the intersection of the two curves occurs, curve 31 lies slightly above curve 32, the reason being that carbon present in the occluded form is not included in the direct carbon analysis.

2. Beyond the "critical" carbon content both curves continue to ascend, curve 32 ascending at a greater rate than curve 31.

Curve 29 represents the total oxygen extracted from the samples, and indicates that for $C < 0.07$ per cent. this is proportional to the amount of carbon extracted, or to the carbon content of the original sample, which is the same in this case. It will be shown later, by metallographic analysis, that in these samples the carbon content is not high enough to insure complete deoxidation. As the original carbon content of the sample is increased, the amount of oxygen absorbed in preparation also increases, but the carbon content is growing proportionally faster, so that after the vacuum treatment a smaller and smaller amount of oxygen remains in the sample, as is also indicated by metallographic examination. At the "critical" carbon content the amounts of oxygen and carbon are just sufficient to combine without leaving any excess of either. Above this point the amount of oxygen, although still increasing, is not high

enough to decarburize the iron completely, consequently the degasified sample contains an excess of carbon.

In this connection, it may be mentioned that an iron-carbon alloy, from another series (not discussed here), prepared in the bell jar furnace, has better magnetic properties than any so far obtained for unalloyed iron. Apparently in this case we have approached very closely to the

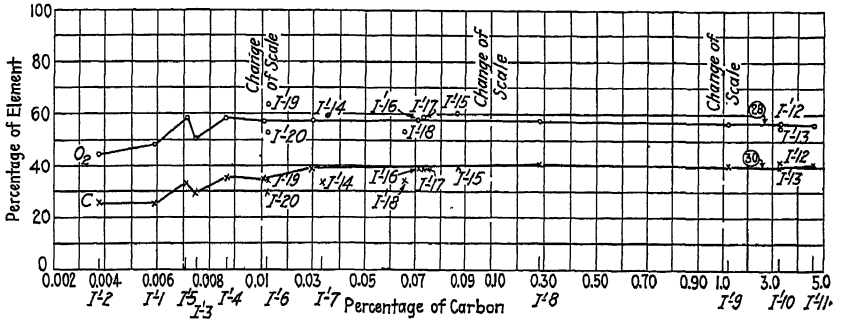


FIG. 5.—CARBON AND OXYGEN PERCENTAGE (BY WEIGHT) OF TOTAL GAS VS. CARBON CONTENT OF SAMPLE.

critical carbon content and have obtained a sample low in oxygen as well as in carbon. Indications are that oxygen is equally as detrimental to magnetic quality as is carbon.[3]

GAS ANALYSIS VS. CARBON ANALYSIS

Consider an alloy of a certain carbon content, say I′-8. Draw a line X parallel to the ordinate (Fig. 4). This vertical line intersects

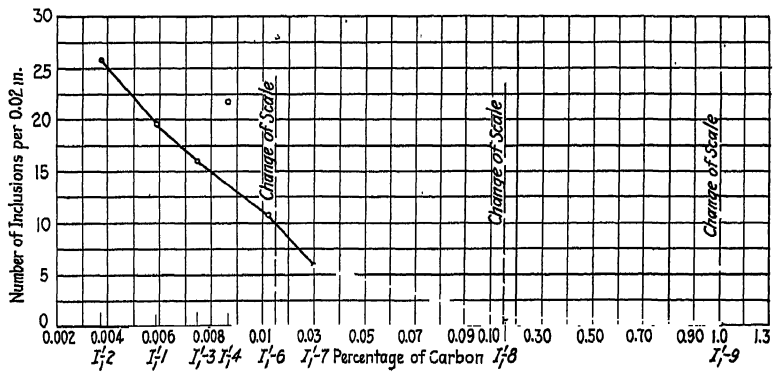


FIG. 6.—NUMBER OF INCLUSIONS PER UNIT AREA OF POLISHED SURFACE VS. CARBON CONTENT.

curves 31, 32 and 33 at points C, A and B, respectively, and the abscissa at point E. Consequently, we have theoretically $AE - CE = BE$, or

[3] T. D. Yensen: What is the Magnetic Permeability of Iron? *Jnl.* Franklin Inst. (1928) **206**, 503, 509.

$AC = BE$. The numerical values do not check this relationship exactly but the difference is so small that it can safely be explained on the basis of experimental error. This holds true for any iron-carbon alloy of this series. In the case of the "critical" carbon content, marked by the letter Y, the points A and C, and B and E coincide, indicating that the original carbon content of the sample is equal to the carbon extracted in the form of gases during the degasification, and that the residual carbon left in the sample after the vacuum treatment is equal to zero. As has been stated before, below the "critical" carbon content the residual sample contains a certain amount of oxygen, and above it, a certain amount of carbon. For this particular series the "critical" carbon content is between 0.03 and 0.10 per cent. C. For alloys prepared by other methods, it may be very different. The important point is that by properly balancing carbon and oxygen, both of them can be substantially eliminated by melting in vacuum.

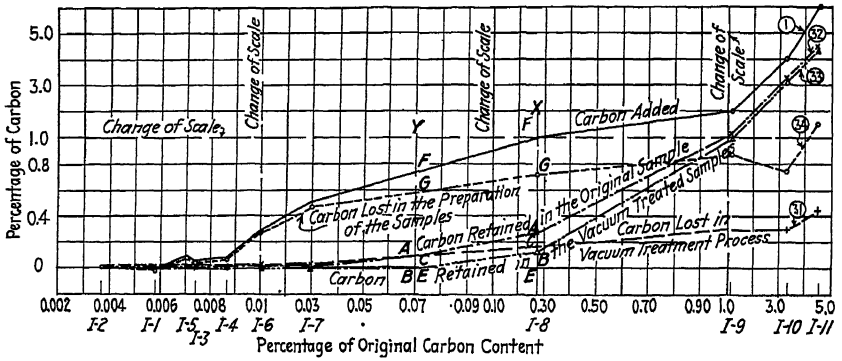


FIG. 7.—CARBON AT VARIOUS STAGES VS. ORIGINAL CARBON CONTENT.

In Fig. 7 the same curves have been plotted to a smaller scale, and in addition the following two curves:

Curve 1, representing the carbon originally added to the electrolytic iron.

Curve 34, representing the carbon lost in the preparation of the samples in air atmosphere.

If a vertical line is drawn, representing the same alloy "X," as in Fig. 4, in addition to the above points A, B, C and E, we have point F, representing the intersection of the vertical line with curve 1, and G with curve 34. Consequently the following relationship holds for all carbon contents: $FE - AE = AG = GE =$ carbon lost by oxidation during the process of preparation of the samples in air atmosphere.

By computing oxygen and carbon as percentages (by weight) of the total gaseous mixture obtained during the vacuum treatment, and by

plotting these results for every sample, using the carbon content of the original sample as abscissa, the result will be two curves shown in Fig. 5. For very low carbon both curves have a small rise up to about 0.01 per cent. C, after which both of them become nearly straight horizontal lines, as would be expected from the fact that 90 per cent. of the gases is CO for C > 0.03 per cent.

Metallographic Examination

All degasified laboratory samples, with the exception of I'_1-5, have been examined microscopically. In the polished samples I'_1-2 to I'_1-9, inclusive, before they were etched, the number of inclusions per unit area seen at the magnification of 200 dia., has been counted for each sample, and plotted against the carbon content of the original sample, giving as a result the curve of Fig. 6. All points, with exception of I'_1-4, lie on a smooth curve, asymptotic to the abscissa. Since it is improbable that an appreciable amount of impurities other than oxygen be present in alloys prepared of electrolytic iron and pure graphite, it is safe to assume that at least 90 per cent. of the inclusions observed through the microscope are oxides. In I'_1-7, the C content of which, according to the above, is the nearest of all the alloys to the "critical" one, we still see an appreciable number of inclusions. Sample I'_1-8 on the other hand, having a very small amount of inclusions, has a considerable excess of carbon. The "critical" carbon content, therefore, must be somewhere between the carbon contents of these two samples, namely 0.03 and 0.10 per cent., perhaps halfway between the two. This will be further investigated.

Commercial Alloys

The question has been raised whether the results of the above series of experiments are applicable only to the particular series of laboratory samples of iron-carbon alloys, or whether they also hold for commercial steels and cast irons. For this reason a series of commercial alloys shown in Table 2 has been obtained and investigated. (See also Table 1).

The following points may be of interest in connection with the work on these alloys (see Table 1):

1. Water vapor was obtained from the steels in amounts of about the same order as from the laboratory alloys, whereas no water vapor was obtained from the samples of cast iron. This is in agreement with the results obtained with the laboratory alloys.

2. The percentage values obtained for CO and CO_2, with a few exceptions, check fairly well the results for laboratory samples.

3. The values obtained for oxygen are somewhat higher than those obtained for the laboratory alloys, but they are still small compared with CO and CO_2.

TABLE 2.—*Commercial Alloys Investigated by Gas Analysis*

No.	Nature	Source	Chemical Analysis								
			Fe	C	Mn	P	S	Si	Cu	Ni	Cr
I'-12	Cast iron, exceptionally high mechanical properties. Cupola furnace product.	Obtained from A. A. Frey		3.00 3.25	0.60 0.80	0.200	0.100	2.25 2.50			
I'-13	Cast iron gasoline engine piston.	Obtained from A. M. Lee		3.24	0.72	0.363	0.085	2.52			
I'-14	2½-in. nails.			0.036							
I'-15	2½-in. square billet open, effervescent heat No. 5088. No deoxidizer used.	Obtained by P. H. Brace from Pittsburgh Steel Co.	99.300	0.13	0.44	0.012	0.028	0.007	0.040	0.051	0.021
	Spoon test of same sample.			0.154	0.230	0.011	0.029	0.005	0.083		
I'-16	2½-in. square billet killed with aluminum. Heat No. 5866.	Obtained by P. H. Brace from Pittsburgh Steel Co.	99.965	0.13	0.46	0.026	0.046	0.100	0.043	0.083	0.021
	Spoon test of same sample.			0.154	0.230	0.012	0.029	0.100	0.083		
I'-17	5/16-in. wire welding, coated. Heat No. 1836. Standard welding wire.	Obtained by P. H. Brace from Pittsburgh Steel Co.		0.10 0.14	0.30 0.50	0.02 and under	0.035				
I'-18	Same heat as I'-17, bare.	Obtained by P. H. Brace from Pittsburgh Steel Co.		0.14	0.50	0.02 and under	0.035				
I'-19	5/16-in. wire welding, not coated bare; heavy steel. Heat No. 6846.	Obtained by P. H. Brace from Pittsburgh Steel Co.		0.05	0.15 and under	0.02	0.035				
I'-20	Same heat as I'-19, but coated.	Obtained by P. H. Brace from Pittsburgh Steel Co.		0.05	0.15 and under	0.02	0.035				

4. Hydrogen was found in all the steel samples, with the exception of I'_1-20, but not in the case of the cast iron samples. A possible explanation of this is that in the laboratory furnace, as well as in the cupola, there is less opportunity for the product to absorb hydrogen than in the case of the open-hearth furnace.

5. The values obtained for the nitrogen content, with the exception of I'-13, which is somewhat high, are all of the same order as the values obtained for the laboratory samples. The source of nitrogen is probably occluded air.

6. All values have been computed for the commercial alloys in the same manner as for the laboratory samples, and some of them have been plotted in Figs. 1 to 5. Remembering that the commercial alloys were prepared under widely differing conditions, and that some of them have passed through various heat treatments, besides hot and cold working, before being analyzed for gases, it is obvious that an exact check cannot be expected under any circumstances, and that the results obtained check surprisingly well.

7. It is interesting to note that the cast iron of "exceptionally high mechanical properties" contains a considerably higher amount of gaseous elements than the old gasoline engine piston, with which it is very similar in chemical composition. Apparently, either oxygen does not have much influence on the mechanical properties of cast iron, or a very high quality material is used in making the gasoline engine piston tested.

Summary

1. A series of laboratory iron-carbon alloys, ranging from 0.0038 to 4.45 per cent. carbon, as well as some commercial steels and cast irons have been investigated for gas evolution by vacuum melting.

2. Water vapor is given off by low-carbon laboratory alloys and by steels, but not by high-carbon alloys and cast irons. The amount is very small.

3. Carbon dioxide is evolved in relatively small quantities in all samples.

4. Carbon monoxide is the principal constituent of the gaseous mixtures in all cases. The amount increases very rapidly with the increase of carbon in the original sample.

5. Free oxygen is given off by all samples in negligible quantities.

6. Hydrogen is not evolved by the laboratory samples and by the cast iron, but to a small extent by open-hearth steel.

7. A certain iron-carbon alloy (about 0.07 per cent. carbon for this particular series) contains just enough carbon and oxygen to be very nearly decarburized and deoxidized by the vacuum melting, as judged from the results of the chemical analysis, and the metallographic examination.

8. Commercial alloys have the same characteristics, as far as gas evolution is concerned, as the laboratory samples of the same carbon content.

9. The number of inclusions decreases uniformly with the increase of the carbon content.

ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to the Westinghouse Electric & Manufacturing Co. in whose research laboratory this work was done, for permission to publish the results. Thanks are due to Dr. T. D. Yensen and O. W. Ellis for their encouragement in the work, and to Messrs. Brace, Frey and Lee for the commercial samples employed.

DISCUSSION

W. HESSENBRUCH, Düsseldorf, Germany (written discussion).—In spite of the contrary opinion of the author, there is no doubt that the gases result, for the most part, as a product of the reaction of the crucible with the carbon content of the steel. The decrease in pressure at the end of the experiment is probably due to an adsorption of the gases on the metallic coating, which the author mentions particularly. The fact that the gas contents of the laboratory melts almost agree with those in commercial steels strengthens the opinion that the apparatus is defective. It would interest me to learn what increase in silicon and aluminum could be determined in the vacuum melts as compared with the initial material.

L. JORDAN and H. C. VACHER, Washington, D. C. (written discussion).—The author of this paper, defending his method of gas analysis against previous criticism, claims to have "established beyond doubt,—that all the gases dealt with come from the metallic charge" and also states that "the suggestions that the gases are due to the reactions between the metallic charge and the refractory material has no valid basis."

In our discussion[4] of the earlier paper by Brace and Zeigler, which described the method of analysis employed in the present work, we made the suggestion as to the source of oxygen in gases evolved from iron-carbon alloys which were melted in vacuum in oxide crucibles. There is nothing in the present paper which in any way supports the claim of the author that there is no valid basis for a similar criticism of his present results.

The results presented by the author in Table 1 (and curve 29, Fig. 4) for per cent. by weight of oxygen in synthetic iron-carbon alloys show increasing oxygen with increase of carbon in the alloys, or in other words they appear to represent a solubility of oxygen in molten iron containing 4.45 per cent. carbon (Sample I'-11) of some 60 times the solubility of oxygen in molten pure iron (Sample I'-2) when both samples of iron are melted under similar conditions. Results which are so at variance with the well known deoxidizing action of carbon in steelmaking and with the available data on the equilibrium concentrations of carbon and oxygen in molten iron-carbon alloys[5] are difficult to accept and, even in the absence of any other objections, cannot

[4] *Proc.* Inst. Metals Div., A. I. M. E. (1928) 564.

[5] A. L. Feild: Physico-Chemical Phenomena from Melt to Ingot. *Trans.* Faraday Soc. (1925) **21**, 255, Table 1.

C. H. Herty, Jr. et al.: Physical Chemistry of Steel-Making—The Solubility

but raise a question as to the accuracy of the observations.

The author emphasizes the following two points as completely disproving our objections to his method of determining oxygen in iron-carbon alloys:

1. The apparent definite end-point in gas evolution from an iron-carbon sample fused in vacuum in a porcelain crucible.

2. A high-carbon sample, once in the condition of apparent freedom from gases as determined above, can be remelted in a new porcelain crucible without evolution of gas in excess of the blank correction.

1. The author was able to reach a point in the vacuum fusion of even high-carbon samples contained in oxide crucibles at which the evolution of gases from the bell jar vacuum furnace practically ceased. The iron samples still contained carbon, sometimes as high as 4.0 per cent. carbon, and it is the author's contention that as long as either carbon remained in the metal or oxygen remained in the crucible refractories, the reduction of the oxides of the crucible would have continued if any such reaction had taken place at all.

In our opinion the reduction of crucible refractories quite certainly did continue even after evolution of gas from the bell jar furnace ceased. Such a condition may develop from the reaction of certain metallic vapors immediately above the molten sample with the gases within the furnace. There may even be present a sufficient amount of this vapor to clean up in the form of nonvolatile oxides and carbon or carbides, all of the oxides of carbon present or being produced by any other reaction within the furnace. Hence, cessation of gas evolution from the vacuum furnace is not a sufficient criterion of the absence of gas-producing reactions.

It has been known for some time that manganese, the most volatile metallic constituent of ordinary steels, may cause serious errors in vacuum fusion analyses for oxygen.[6] In the course of the further development and improvement of the original Bureau of Standards vacuum fusion method it has been necessary to make a study of the nature of this interference.

This work has shown that in vacuum fusion methods in which the sample is melted under very low pressures the error caused by manganese is due almost entirely to the reaction between manganese vapor and carbon monoxide to give MnO and carbon (or carbide). It has often happened that, in the case of high manganese alloys known to contain considerable amounts of oxygen, attempted analyses have shown a total evolution from the furnace of even less oxygen than the amount known to represent the true blank of the apparatus. Under certain conditions, therefore, manganese vaporizing from the molten sample may clean up practically all gases present or being produced by reactions within the furnace.

In the paper under discussion there is no reason to suspect manganese of playing the part outlined above, but there is reason to suspect aluminum of acting in a manner wholly equivalent to manganese. The paper states that the iron-carbon alloys were melted in the vacuum treatment in "high refractory porcelain crucibles." Presumably these are the same as the special ware composed of pure fused alumina bonded with aluminum silicate as described by Brace and Ziegler in their original paper on this method.

---

of Iron Oxide in Iron. Min. & Met. Investigations, *Bull.* **34,** Carnegie Inst. Technology (1927) Fig. 10.

[6] W. Hessenbruch and P. Oberhoffer: Ein verbessertes Schnelverfahren Zur Bestimmung der Gase in Metallen, insbesondere des Sauerstoffs im Stahl. Archiv. Eisenhuttenwesen (1928) **1,** 583.

R. vonSeth: *Jernkontorets Ann.* (1928) **112,** 113. Abstract in *Stahl und Eisen* (1928) **48,** 1374.

In connection with our own work on manganese interference in the vacuum fusion method we have made the following tests on the interference of aluminum. These tests also clearly show once again the comparative ease with which even fused alumina is reduced by a molten iron-carbon alloy. We prepared an iron-carbon alloy by melting together electrolytic iron and graphite. A 100-gram sample of this alloy containing 4.1 per cent. carbon was remelted in an alundum crucible in a vacuum high-frequency induction furnace. The vacuum melt was held at or somewhat above 1600° C. for 6 hr. with continuous pumping of gases from the furnace. After this treatment the melt contained 1.4 per cent. carbon and 2.5 per cent. aluminum. The loss in carbon, 2.7 per cent., represents a reduction from the crucible of aluminum equivalent to 4 per cent. of the melt. Therefore 1.5 per cent. aluminum was volatilized from the melt and was available for the reduction of carbon monoxide present in the furnace. That it did so react was evidenced by a very voluminous accumulation of alumina and carbon on the inside walls of the alundum crucible immediately above the surface of the melt. No metallic aluminum could be detected in this deposit.

As still further proof of the action of aluminum in preventing the recovery of oxygen in a vacuum fusion analysis, a sample of an open-hearth iron, known to contain 0.06 per cent. oxygen, was analyzed by our regular vacuum fusion procedure, except that there was simultaneously present in the graphite crucible a 20-g. sample of the aluminum-carbon-iron alloy. Under these conditions oxygen equivalent to only 0.03 per cent. of the open-hearth iron sample was recovered, that is, 50 per cent of the oxygen was retained in the furnace by the aluminum vapor.

The apparent end-point in gas evolution reached by the author of this paper we believe is to be explained on the basis of conditions similar to those described above and does not represent the completion of removal of gas from his sample, nor the absence or cessation of reduction of his crucible, but simply the establishment of conditions which do not permit removal of gases from the vacum furnace.

2. The second point made by the author against the existence of reactions with the porcelain crucibles is that if a sample of an iron-carbon alloy which has once reached the so-called end-point of gas evolution is again melted in a new porcelain crucible no evolution of gas from the vacuum furnace in excess of the blank correction is observed.

It is at once evident from the preceding discussion that this condition may be brought about by the composition of the sample and is not at all an evidence of the absence of reduction of crucible oxides.

We are, therefore, still in complete disagreement with the author in his statement that no valid basis exists for suspecting reactions between the metallic charge and the refractory materials and we must continue to regard the method of analysis employed in the present paper as entirely inapplicable to the determination of oxygen in iron-carbon alloys.

H. W. GILLETT, Washington, D. C. (written discussion).—The comments of Jordan and Vacher on the unsuitability of Ziegler's method of melting in refractory oxide containers for quantitative analysis of total oxygen in metals and on the lack of reliability of analyses so made, are, to my mind, fully justified. I do not believe that Mr. Ziegler can wave a magic wand over his melt and prevent the reduction of the refractory oxides by the carbon of the melt in Pittsburgh. Reduction takes place in Long Island City, in Washington and in Aachen as was clearly brought out in the discussion of Brace and Ziegler's 1928 paper.

However, the complete disagreement of all other workers' in the field with Ziegler's procedure as an analytical method should not blind us to the evidence he produces

as to the very great possibilities in vacuum melting of steel. As Yensen pointed out a dozen years ago,[7] and as is obvious to everyone, the reaction

$$FeO + C \leftrightharpoons Fe + CO$$

goes toward the right as long as CO is removed.

Herty's work on the formation and the effect of nonmetallic inclusions in steel at the Pittsburgh station of the U. S. Bureau of Mines should make us still more alive to the possibilities of deoxidation by a deoxidizer which leaves no solid nonmetallic inclusions in the metal.

It does not appear at all out of the range of commercial possibilities today to build an Ajax Northrup type of high-frequency steel melting furnace with a 1-ton capacity and go on up from that to still larger furnaces, and to operate them with melting costs not far from those of arc-furnace practice.

It also appears entirely feasible to cap such a furnace during the finishing of the heat, connect a vacuum pump and, without going to the very low pressures of the laboratory experiments, so reduce the pressure that the CO concentration over the melt is diminished and, in consequence, FeO is also greatly diminished. A low-carbon steel, under reduced pressure, will be deoxidized to an extent comparable to that of a high-carbon steel under atmospheric pressure, requiring less final deoxidation and having greater freedom from inclusions, just as is indicated by Ziegler's Fig. 6.

The simultaneous elimination of oxygen and carbon is interesting in iron for magnetic purposes, but increased elimination of FeO from low-carbon steel as CO, instead of merely changing it into oxides of silicon, manganese and aluminum which decline to eliminate themselves from the steel, is still more interesting.

It seems surprising that quality steelmakers are not energetically following up vacuum melting, now that man-sized furnaces of the Ajax Northrup type are in sight, and Mr. Ziegler's paper should encourage them to follow it up promptly.

C. G. Fink, New York, N. Y. (written discussion).—In the introduction, second paragraph, the author says: "The writer does not wish to create the impression that . . . the gases obtained are present as such in the original sample." And yet in the Summary, item 2, "Water vapor is given off by low-carbon laboratory alloys." Is it not possible that this water vapor is the result of interaction between the oxygen or oxide present in the metal and absorbed or dissolved hydrogen?

The author records that Niagara Falls Electrolytic Iron Co.'s electrolytic iron contained 0.448 per cent. oxygen. Was the sample so called air-annealed, or was it a sample of iron directly off the mandrel before heating?

On page 430, near the middle of the page, "In every case there was a marked and rather sudden improvement in the furnace vacuum, always coincident with the formation of a heavy black deposit on the inside of the bell jar." Was this deposit lampblack? If so, would it not act like cocoanut charcoal, as a very good adsorbent, and hence the good vacuum?

On page 437, the author records that "it is safe to assume that at least 90 per cent. of the inclusions observed through the microscope are oxides;" and on page 439, "Carbon monoxide is the principal constituent of the gaseous mixtures in all cases. The amount increases very rapidly with the increase of carbon in the original sample." Accordingly, would it not be well to add that this carbon monoxide is largely a product of the reaction of the oxides present with the carbon? As the statement now stands in the summary, the reader concludes that all of this CO is in the metal . . . but perhaps this is what Dr. Ziegler found.

---

[7] T. D. Yensen: Preparation of Pure Alloys for Magnetic Purposes. *Trans.* Amer. Electrochem. Soc. (1917) **32**, 179.

C. H. HERTY, JR., Pittsburg, Pa. (written discussion).—Did the test pieces lie quiet in the mold or were they blowy? With as much gas as the author reports, one would expect to find the tests full of blowholes unless there was some element present that held the gas in solution. Were any efforts made to indentify the inclusions, other than simply to observe them under the microscope? It is hard to visualize enough iron oxide in higher carbon steels to show globular inclusions, as mentioned in the paper.

J. M. GAINES, JR., Pittsburgh, Pa. (written discussion).—I am rather surprised at some of the author's findings, particularly the relation of carbon to gas content of the laboratory samples. The gases may have originated during preparation of the samples in one or more of several ways—from the crucible material, which is very improbable on account of the oxidizing atmosphere in which melts were made; from the iron, which contains 0.026 per cent. gases by weight; from the atmosphere; or from the Acheson graphite used in carburizing the iron. Since the weight of iron, the atmospheric pressure and the time of melting are substantially constant in each case, the variation in gas content must be due to gas introduced with the graphite.

This is not at all unlikely. Mr. Ziegler notes that a graphite crucible, which he degasified at white heat, evolved tremendous quantities of gas and required a long time to reach a pressure of 0.08 mm. of mercury. It is well known that various forms of carbon adsorb gases tenaciously. It therefore seems reasonable to suppose that the gases extracted from these alloys were originally adsorbed on the graphite carburizer and subsequently dissolved in the iron melt. This would conveniently account for the proportionality between the carbon content and the gas content.

We use electrolytic iron constantly and I have noticed one thing about it which may bear on the present case. If a charge is melted in air in the induction furnace and cast immediately it will tend to show blowholes and to effervesce in the mold. However, after being held molten for an hour or two it will pour and solidify from the bath, cold-rolled into strips and cleaned in 20 per cent. alcoholic quietly. It appears that the process of diffusion of gases through liquid metals is rather slow compared to that of the metaloids. This would indicate that the 10-min. period during which Mr. Ziegler kept his samples liquid would be insufficient to permit escape or absorption of appreciable quantities of gas to or from the atmosphere. Furthermore, the fact that two days were necessary for complete degasification of the 6 per cent. carbon sample *in vacuo* is evidence of the slowness of the reaction.

Mr. Ziegler would confer a favor by clearing up this point—either by using degasified graphite as a carburizer or by varying the molten period in preparing his samples—up to 2 or 3 hr. if possible.

N. A. ZIEGLER (written discussion).—The author wishes to express his appreciation to all who contributed to the discussion of his paper, and in this way have helped to further the work by bringing out many interesting and important points. In particular, thanks are due to Dr. Hessenbruch, Messrs. Jordan and Vacher, and Dr. Gillett. Their contributions have suggested a number of new experiments, some of which are still in progress.

In answering Dr. Fink's questions, it may be stated that the author has exactly the same explanation as to the presence of water vapor and carbon monoxide in the resultant gaseous mixture as Dr. Fink suggests; namely, that they are the product of interaction of oxide present in the metal, and absorbed or dissolved hydrogen and carbon respectively. The expressions "Water vapor is given off" and "carbon monoxide is the principal constituent of the gaseous mixture" were used for the sake of simplicity after having introduced the sentence, "The writer does not wish to create the impression that—the gases obtained are present as such in the original sample."

The Niagara Falls Electrolytic Iron Co.'s electrolytic iron was used as it comes from the bath, cold-rolled into strips and cleaned in 20 per cent. alcoholic hydrochloric acid.

The black deposit formed on the inside of the bell jar, to the best of our knowledge, is evaporated and condensed metal, and not lampblack. However, as more recent experiments have shown, it may have something to do with the finishing vacuum.

In answering Dr. Herty's questions, the samples I'-1 to I'-7 were blowy, the samples I'-8 to I'-11 were sound to the naked eye. There were no attempts made as to the identification of the inclusions observable through the microscope. The high-carbon alloys, as can be seen from Fig. 6, had very few of them.

Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-nitrogen

By R. S. Dean,* R. O. Day* and J. L. Gregg,* Chicago, Ill.

(New York Meeting, February, 1929)

BLUE HEAT PHENOMENA

In constructing a theory of the flow and hardening of metals, we necessarily make use of such phenomena as seem to be universally observed in metals. It is, therefore, a matter of concern to the constructors of such mnemonic systems if one or two of the group classified as metals show anomalous behavior. Such egregious phenomena are observed in pure or nearly pure iron in the reaction of its mechanical properties to low-temperature annealing after cold work and to increased temperature of testing. In short it has been generally observed that iron, as an outstanding exception among metals, increases its hardness and strength by low-temperature annealing after cold work,[1] and also by increase of testing temperature to the range of 150° to 300° C.

The investigation here recorded was made then with the object of ascertaining if similar phenomena were observed in high-purity iron and, if not, to the presence of which impurities these phenomena could be traced.

Experimental Procedure

Three kinds of iron were taken for a study of hardening by reheating after cold work:

1. Vacuum-melted electrolytic iron; melted in an Arsem furnace in a magnesia crucible. That this iron was of high purity is indicated by a magnetic permeability above 20,000.
2. Electrolytic iron melted in air in a small laboratory furnace.
3. Armco iron, commercial material.

These materials in the form of forged bars, annealed at 980° C. in vacuum, were reduced 30 per cent. in thickness by cold rolling and then reheated to temperatures varying from 100° to 500° C. The Rockwell hardness number was measured after each treatment. The results are shown in Fig. 1, curves 1, 2 and 3.

* Metallurgical Engineers, Western Electric Co., Inc.

[1] C. Y. Clayton: Effect of Annealing upon the Hardness of Cold-worked Ingot Iron. *Trans.*, A. I M. E. (1926) **73**, 926.

It is at once apparent that the vacuum-melted electrolytic iron shows no hardening while the air-melted iron increases markedly in hardness by reheating to 250° C. The Armco iron is intermediate.

A microscopic study of the melted electrolytic irons, 1 and 2, gave the significant pictures shown in Figs. 2 to 4, inclusive. Fig. 2 shows the structure of the high-purity iron. Fig. 3 shows that by melting in

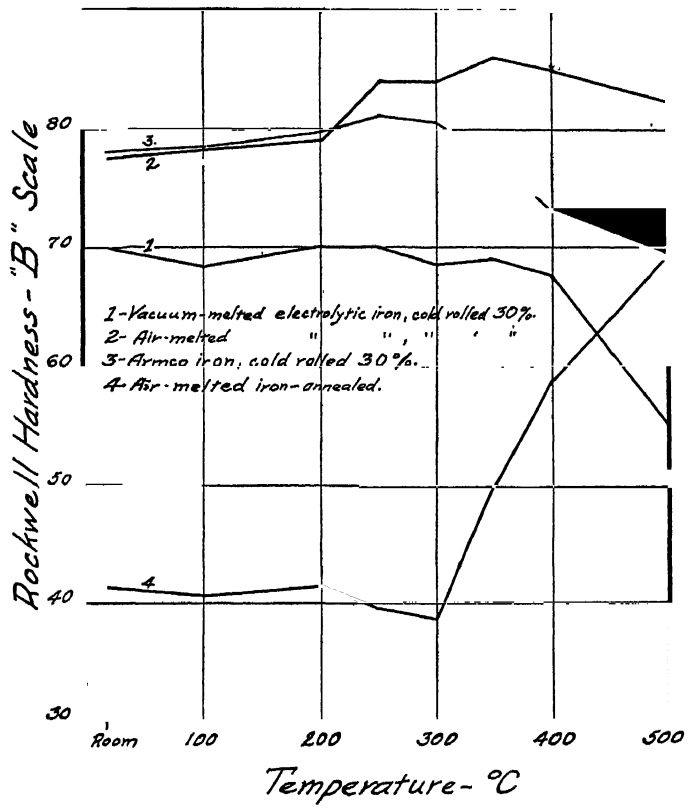


FIG. 1.—EFFECT OF REHEATING ON HARDNESS OF COLD-ROLLED IRONS 1, 2 AND 3, AND ALSO OF ANNEALED IRON 2.

air a very considerable amount of impurity has been taken up, apparently nitride. Fig. 4 shows that by reheating to 500° C. and cooling in air these nitridelike needles disappear.

Analysis of iron 2 showed 0.07 per cent. nitrogen. Samples of vacuum-melted iron 1 treated with ammonia to give an amount of nitride, which judged from the metallographic examination was similar to iron 2, behaved identically with iron 2 as regards hardness changes on heat treatment. The conclusion that the presence of nitrogen was the cause of the hardening accordingly presents itself.

The hardening on low-temperature annealing then might be explained as due to solution of precipitated nitride. In this case the hardening should take place also on reheating the annealed material containing nitride. The observations on this possibility using iron 2 are plotted in curve 4 of Fig. 1. Hardening does take place by reheating the annealed

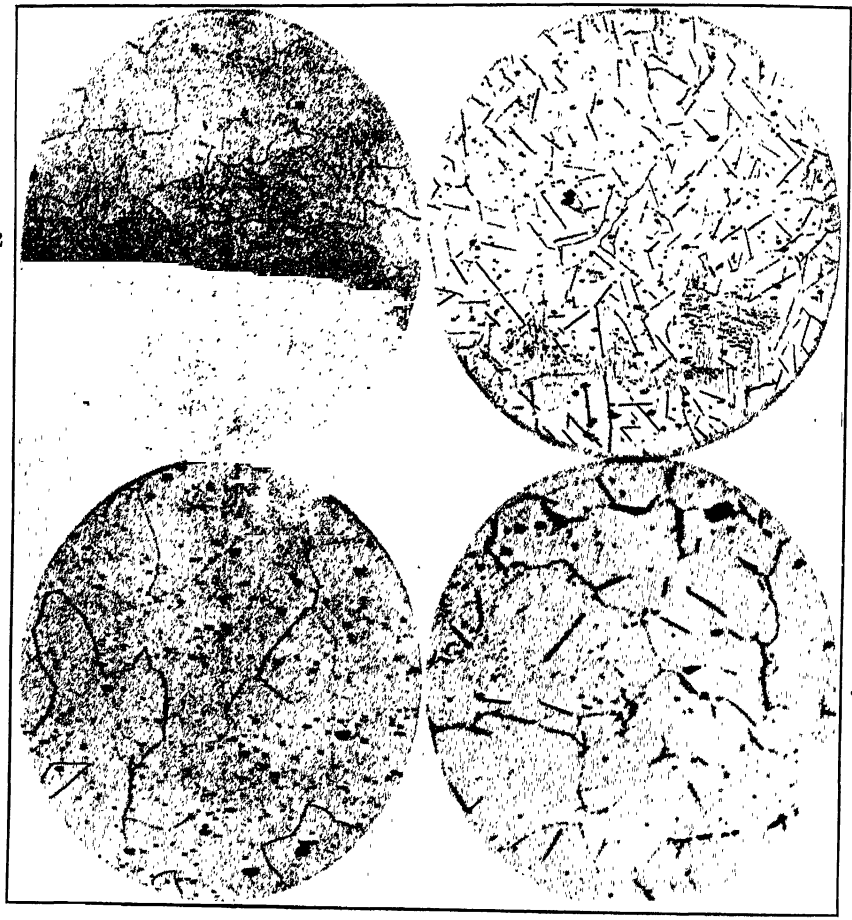


FIG. 2.—ELECTROLYTIC IRON MELTED IN VACUUM, HOT-FORGED FROM INGOT TO BAR AND COLD-ROLLED 30 PER CENT. ×100.

FIG. 3.—ELECTROLYTIC IRON MELTED IN LABORATORY. NOTE MANY NITRIDE NEEDLES. ×100.

FIG. 4.—IRON 2 AFTER QUENCHING FROM 500° C. NOTE ABSENCE OF NEEDLES. × 100.

FIG. 5.—ARMCO IRON NITRIDED BY HEATING IN AMMONIA; ANNEALED IN VACUUM. × 400.

material but not until a temperature of 350° C. is reached; whereas, in the cold-worked material hardening was pronounced at 250° C. If then the two phenomena arise from the same cause, the solution of the nitride must be definitely accelerated by working the metal.

To get additional evidence on whether the hardening by annealing after cold work was a solution phenomenon, we measured the electrical conductivity change accompanying this hardening. For this purpose we used wire made from ¼-in. Armco iron rod nitrided in ammonia. This rod was drawn to 16 gage, annealed in vacuum at 980° C. and then cold drawn to 18 gage. By analysis it showed 0.086 per cent. nitrogen. The metallographic appearance and behavior was similar to iron 2 above. Figs. 5 and 6 show this iron for purposes of comparison with

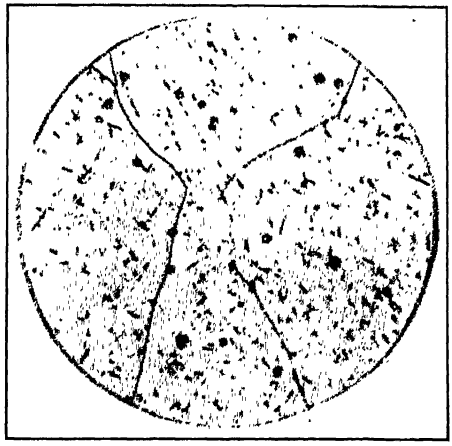


FIG. 6.—IRON 2 QUENCHED FROM 500° C. AND REHEATED TO 350° C. FOR 1 HR.; NITRIDES REPRECIPITATED IN FINER NEEDLES.

Figs. 3 and 4. The 18-gage cold-drawn wire was then heated at 200° C. and at 300° C., and the changes in tensile strength and conductivity were noted. The results follow:

Treatment	Tensile Strength, Lb. per Sq. In.	Resistance, Ohms per Cu. Cm. at 22.9° C.
As drawn	69,000	10.93×10^6
After heating to 200° C for 2 hr	76,000	11.06×10^6
After heating to 300° C. for 2 hr	78,000	11.10×10^6

Hardening by reheating after cold work is accordingly definitely associated with an increase in electrical resistance. This furnishes support to the idea that this hardening is a solution phenomenon.

The question now arises: Is the increase of strength with increase of temperature—the so-called temper brittleness—also absent in pure iron? To determine this point, iron wire was freed from nitrogen by heating it for 12 hr. in hydrogen at 1100° C., and this wire compared with the nitrided wire already described, and also with Armco iron wire

(analysis 0.007 per cent. N_2). The results of these observations are shown in Fig. 7. It will be noticed that in the case of the Armco wire and the nitrogenized wire there is a marked increase in strength in the range 200° to 300° C., which is almost entirely absent in the hydrogen-annealed wire, which in no case gives a value higher than the room-temperature tensile strength.

Temper brittleness is accordingly absent or very slight in nitrogen-free iron and is due apparently to the solution of nitride in the heating and pulling process.

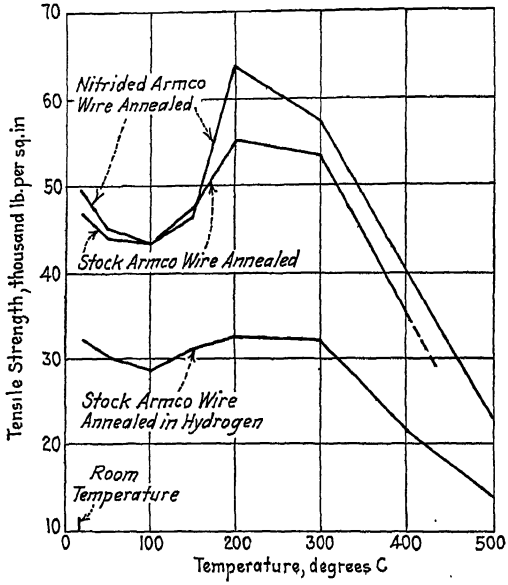


FIG. 7.—TENSILE STRENGTH AT SLIGHTLY ELEVATED TEMPERATURES.

We come now to the conclusion that commercial irons owe their property of hardening by reheating after cold work, as well as their increase in tensile strength in the range 100° to 300° C., to the solution of small amounts of iron-nitride present.

SOLUTION AND DISPERSION HARDENING IN THE SYSTEM IRON-NITROGEN

From the equilibrium diagram of Fry[2] for the system iron-nitrogen (Fig. 8), it is evident as was suggested by Sawyer[3] that dispersion hardening is a possibility. So far as we can find it has not been actually observed. To determine if it could be readily observed, a sample of

[2] Fry: *Kruppsche Monatshefte* (1923) **4**, 137.

[3] C. B. Sawyer: Nitrogen in Steel. *Trans.* Amer. Soc. Steel Treating (1925) **8**, 291; *Trans.*, A. I. M. E. (1923) **69**, 798.

No. 2 iron, discussed in the first section of this paper, was heated to 500° C. and quenched, then reheated at temperatures varying from 100° to 350°

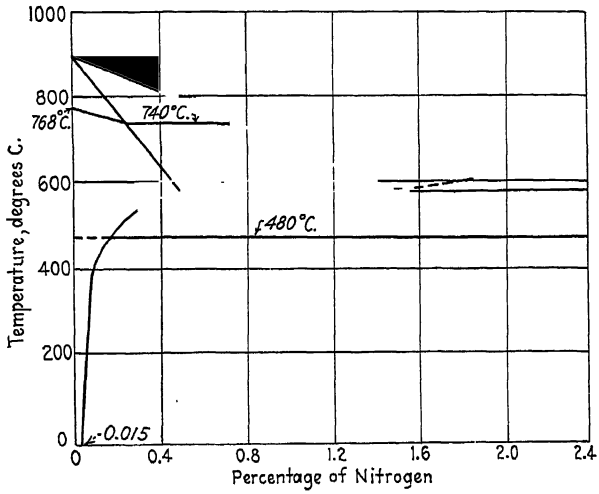


FIG. 8.—IRON-NITROGEN DIAGRAM ACCORDING TO FRY.

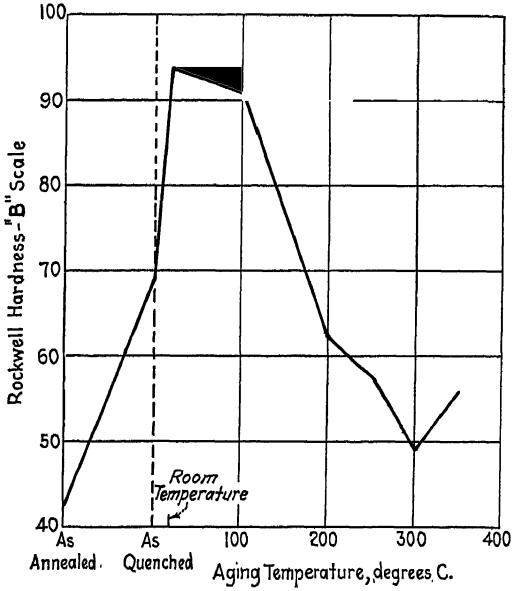


FIG. 9.—EFFECT OF AGING TEMPERATURE ON IRON 2 QUENCHED FROM 500° C. 24 HR. AT ROOM TEMPERATURE AND 1 HR. AT OTHER TEMPERATURES.

C. Rockwell "B" readings were taken immediately after each treatment. The results are shown in Fig. 9.

We see that there is a sharp increase from 40 to 70 Rockwell "B" on quenching, which is due to the solution of the nitride present. There is then a further sharp increase to 95 Rockwell "B" by holding at room

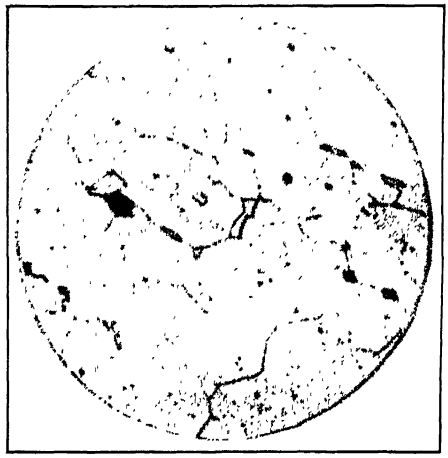


FIG. 10.—SAME WIRE AS IN FIG. 5, AFTER QUENCHING FROM 500° C. NOTE ABSENCE OF NEEDLES. × 400.

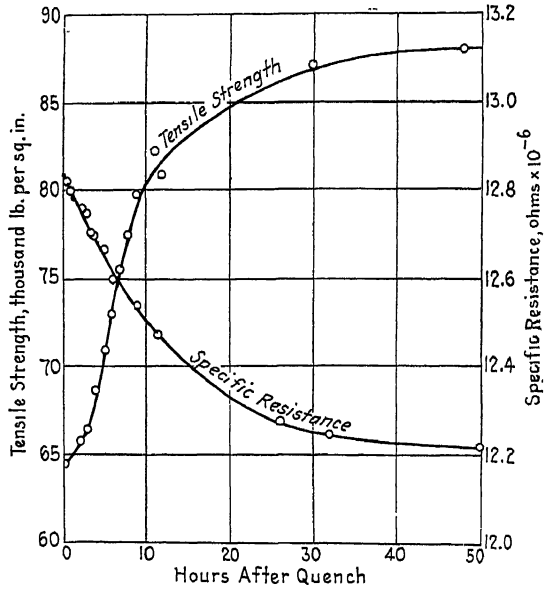


FIG. 11.—CHANGE IN TENSILE STRENGTH AND ELECTRICAL RESISTANCE UPON AGING NITRIDED IRON AT ROOM TEMPERATURE.

temperature 24 hr. Higher temperature-aging results in a decrease due to agglomeration of the nitride until a temperature of 300° C. is reached, when hardening again takes place due to solution.

The system iron-nitrogen is accordingly a room-temperature hardening system and without cold work very little increase of solubility is evidenced below 350° C., but after that temperature is reached there appears to be a sharp increase to 500° C. This is in accordance with Fry's diagram. From these results it would appear that at 300° to 350° C. sufficient agglomeration of the nitride might take place so that the

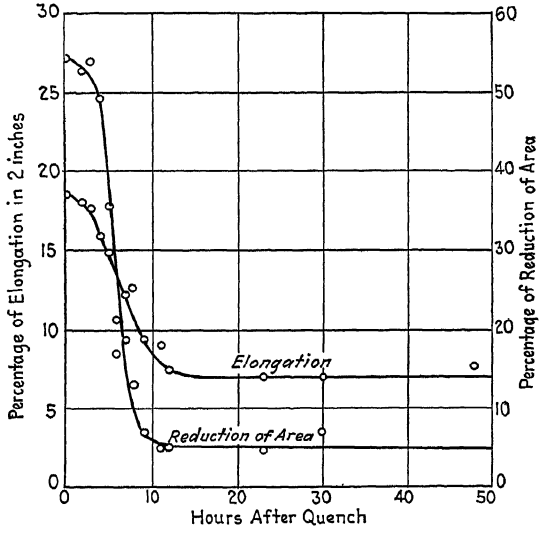


FIG. 12.—CHANGE IN ELONGATION AND REDUCTION OF AREA UPON AGING NITRIDED IRON AT ROOM TEMPERATURE.

particles could be seen under the microscope. This proved to be the case, as shown in Fig. 10.

The course of the conductivity and mechanical property changes during dispersion hardening was then followed in the 0.86 per cent. N wire previously described. The results are shown in Figs. 11 and 12. These show that the iron-nitrogen system behaves in this regard entirely similarly to lead-antimony and other room-temperature hardening alloys. The iron-nitrogen system is then a typical dispersion-hardening system which shows room-temperature hardening in a marked degree.

INDEX

(NOTE: In this index the names of authors of papers and discussions and of men referred] to are printed in SMALL CAPITALS, and the titles of papers in *italics*.)

A

ABORN, R. H.: *Discussion on Pure Iron and Allotropic Transformations*, 342
Africa: iron ore, reserves, 25, 38
ALEXANDER, J.: *Discussions: on Physical Chemistry of Steelmaking*, 240, 251
on Pure Iron and Allotropic Transformations, 344
American Institute of Mining and Metallurgical Engineers: Divisions: Iron and Steel, officers and committees, 4
Medals: Hunt medal award to James Aston, 5
officers and directors, 4
ARMSTRONG, P. A. E.: *Discussion on Metallic Electrodes for Cast-iron Arc Welding*, 158
Asia: iron ore, reserves, 26
ASTON, J.: *New Development in Wrought Iron Manufacture*, 166; *Discussion*, 176, 177, 178
recipient of Hunt medal, 5
ATCHERSON, R. W. H.: *Discussion on Physical Chemistry of Steelmaking*, 241
Australia: iron ore, reserves, 27

B

BAIN, E. C.: *Discussion on Gamma-alpha Transformation in Pure Iron*, 365
Barium carbonate retards fusion of electrode in cast-iron welding, 144
Barium oxide, effect on desulfurizing power of blast-furnace slags, 126
Basic open-hearth practice (*See also* Steelmaking): diffusion of iron oxide from slag to metal, 284
effect of high manganese, 240, 267
effect of silicon in pig iron, 192, 262
elimination of unreduced oxides of pig iron, 179
equilibrium of system iron oxide-carbon in molten iron, experimental data, 304
finishing the heat, 273
foaming, causes and correction, 235, 265
free iron in slag, 207
gases in steel, 254, 278
iron oxide in slag, cause and effect, 271
ladle reactions, 193, 253, 275
limestone, calcining, 262
losses, definition and calculation, 197
Basic open-hearth practice: oxidation of scrap, 260
oxide content compared with that in electric furnace, 317
pig iron, classification, 262
piping in steel, 281
scrap, oxidation, 260
scrap produced, 197, 211, 215
scrap, sulfur absorption, 261
slag action in ladle, 193, 253, 275
slags, typical analyses, 228
sulfur absorption by scrap, 261
yields, definition and calculation, 197
Basic Open-hearth Yields (KING) 197; *Discussion*, 232
BENEDICKS, C.: *Discussion on Gamma-alpha Transformation in Pure Iron*, 364
Blast-furnace Filling and Size Segregation (FURNAS AND JOSEPH) 98; *Discussion*, 124
Blast furnace practice: benefit of sinter, 66
charging methods, influence on size distribution of solid particles, 98
experiments with models, 100
filling and size segregation, 98
gas-solid contact, importance, 98
irregular operation of furnace detrimental to finished steel, 196
screen analyses of Lake ores, 122
700-ton, gas-solid contact in shaft, 84
sintered charge, advantages, 121
size distribution of solid particles, quantitative data, 84
influence of methods of charging and treatment of raw materials, 98
Blast-furnace slag, iron: desulfurizing power affected by barium oxide, 126
affected by viscosity, 139
Bradley process of making manganese ore, 68
operating statistics, 77
Brazil: iron ore, reserves, 20
BUCK, W. E.: *Discussion on Physical Chemistry of Steelmaking*, 242
Byers process, wrought iron, 166

C

Canada: iron ore, reserves, 18
Cast iron: welding, arc, with coated wrought-iron electrodes, 144, 161
Change in Microstructure of Iron at A_3 Transformation Point (ROGERS) 370; *Discussion*, 380

Charter Party, transportation provisions, 31
Chile: iron ore, reserves, 20
China: iron ore, reserves, 26, 36
CHOU, C. H. AND SAUVEUR, A.: *The Gamma-alpha Transformation in Pure Iron*, 350; *Discussion*, 369
Coatings, on metals, possible observation of spreading behavior by use of equipment for observing change in microstructure of iron, 381
Cuba: iron ore, reserves, 19

D

DAY, R. O., DEAN, R. S. AND GREGG, J. L.: *Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-nitrogen*, 446
DEAN, R. S.: *Discussion on Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron*, 313
DEAN, R. S., DAY, R. O. AND GREGG, J. L.: *Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-nitrogen*, 446
DEJEAN, P.: *Discussion on Gamma-alpha Transformation in Pure Iron*, 365
Diffusion of Iron Oxide from Slag to Metal in the Open-hearth Process (HERTY) 284; *Discussion*, 299
DOAN, G. E.: *Discussion on Gamma-alpha Transformation in Pure Iron*, 366
DORNIN, G. A.: *Discussion on Diffusion of Iron Oxide from Slag to Metal in the Open-hearth Process*, 302

E

Effect of Barium Oxide on the Desulfurizing Power of Blast-furnace Slags (WOOD AND JOSEPH) 126; *Discussion*, 142
EGAN, J. J. AND KINZEL, A. B.: *Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron*, 304
England: iron ore, reserves, 22
EPSTEIN, S.: *Discussion on Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron*, 316, 319
Europe: iron ore, reserves, 22
Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron (KINZEL AND EGAN) 304; *Discussion*, 311

F

Fayalite in sinter, structure, 57
FEILD, A. L.: *Discussion on Physical Chemistry of Steelmaking*, 233 et seq.
FINK, C. G.: *Discussion on Gases Extracted from Iron-carbon Alloys by Vacuum Melting*, 443
FITTERER, G. R.: *Discussion on Pure Iron and Allotropic Transformations*, 343
Foreign Iron Ores (HART) 7; *Discussion*, 36
FORKUM, C. S.: *Discussion on Effect of Barium Oxide on the Desulfurizing Power of Blast-furnace Slags*, 142
FOSS, F. F *Discussion on Foreign Iron Ores*, 36
France: iron ore, reserves, 23
FRANCHOT, R.: *Discussion on Physical Chemistry of Steelmaking*, 252
Furnace: for observing wave change in microstructure of iron at A3 transformation point, 371, 380
possible application to study of coatings, 381
Sarbey, description, 305
FURNAS, C. C.: *Discussion on Blast-furnace Filling and Size Segregation*, 125
FURNAS, C. C. AND JOSEPH, T. L.: *Blast-furnace Filling and Size Segregation*, 98
FURNAS, C. C. AND KINNEY, S. P.: *Gas-Solid Contact in the Shaft of a 700-ton Blast Furnace*, 84

G

GAINES, J. M., JR.: *Discussions: on Experimental Data on the Equilibrium of the System Iron-Oxide carbon in Molten Iron*, 311
on Gases Extracted from Iron-carbon Alloys by Vacuum Melting, 444
on Physical Chemistry of Steelmaking, 252, 257
GAINES J. M. JR. AND HERTY, C. H. JR.: *Unreduced Oxides in Pig Iron and Their Elimination in the Basic Open-hearth Furnace*, 179
Gamma-alpha Transformation in Pure Iron (SAUVEUR AND CHOU) 350; *Discussion*, 361
Gas-solid Contact in the Shaft of a 700-ton Blast Furnace (KINNEY AND FURNAS) 84; *Discussion*, **M29**, 138
Gases Extracted from Iron-carbon Alloys by Vacuum Melting (ZIEGLER) 428; *Discussion*, 440
GASES in metals: extracted from iron-carbon alloys by vacuum melting, 428
iron-carbon alloys, causes, 428, 440
study with high-vacuum induction furnace, 428
Germany: iron ore, reserves, 22
GILLETT, H. W. *Discussions: on Experimental Data on the Equilibrium of the System Iron Oxide-carbo in Molten Iron*, 314
on Gases Extracted from Iron-carbon Alloys by Vacuum Melting, 442
on Pure Iron and Allotrophic Transformations, 334
GREGG, J. L., DEAN, R. S. and DAY, R. O.: *Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-nitrogen*, 446

H

Hadfield's manganese steel, studies with high-power microscope, 382

HALL, J. H.: *Studies of Hadfield's Manganese Steel with the High-power Microscope*, 382
photograph, 6
HART, C.: *Foreign Iron Ores*, 7
HAYES, A.: *Discussions: on change in Microstructure of Iron at As Transformation Point*, 381
on Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron, 316, 317, 318, 319
on Physical Chemistry of Steelmaking, 257
on Pure Iron and Allotropic Transformations, 339
Hematite in sinter, structure, 53
HERTY, C. H., JR.: *Diffusion of Iron Oxide from Slag to Metal in the Open-hearth Process*, 284; *Discussion*, 299, 301, 302
HERTY, C. H. JR.: *Open-hearth Operation from the Chemical Viewpoint*, 260
Discussions: on Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron, 315, 316, 317, 318
on Gases Extracted from Iron-carbon Alloys by Vacuum Melting, 444
on New Development in Wrought Iron Manufacture, 178
on Physical Chemistry of Steelmaking, 235 et seq.
HERTY, C. H. JR. AND GAINES, J. M. JR.: *Unreduced Oxides in Pig Iron and Their Elimination in the Basic Open-hearth Furnace*, 179
HESSENBRUCH, W.: *Discussion on Gases Extracted from Iron-carbon Alloys by Vacuum Melting*, 440
HIBBARD, H. D.: *Discussions: on New Development in Wrought Iron Manufacture*, 176
on Physical Chemistry of Steelmaking, 240
HOBLEY, A. H.: *Discussions: on Foreign Iron Ores*, 36
on Manganese Ore by the Bradley Process, 82, 83
Howe Memorial Lecture (Hall), 382

I

Iron, cast. *See* Cast Iron.
dirty, causes, 179, 270
molten, equilibrium of system iron oxide-carbon, experimental data, 304
pig. *See* Pig Iron.
pure, allotropic transformations, 320
definition, 320
gamma-alpha transformation, 350
wave change in microstructure at As transformation point, 370
relation of nitrogen to blue heat phenomena, and dispersion hardening in system iron-nitrogen, 446
wave change in microstructure at *As* transformation point, 370
wrought. *See* Wrought Iron.
Iron-carbon alloys: diagram, evolution, 321
gases, cause, 428, 440
gases extracted by vacuum melting, 428
Iron-nitrogen system: dispersion hardening, 450
Iron ore: Bradley process of obtaining, 69
Iron-ore reserves: Africa, 25, 38
Asia, 26
Australia, 27
Canada, 18
China, 26, 36
Cuba, 19
England, 22
France, 23
Germany, 22
Japan, 26
laterite, 27
Luxemburg, 23
Mexico, 19
Newfoundland, 18, 38
Russia, 36
South America, 20
Spain, 24
Sweden, 24
United States, 16, 33, 36, 38
Iron-ore Sinter (SCHWARTZ) 39; *Discussion*, 66
Iron-ore sinter: Bradley process, 68
microscopic study, 43
structure and composition, 39
Iron ores: analyses, world, 8
foreign, analyses, 10
extent and character, 7
transportation, 29
laterite, reserves, 27
merchandising, 32
sintering, fundamental reactions, 39
resulting minerals, 39
transportation, 30
Charter Party provisions, 31

J

Japan: iron ore, reserves, 26
JOHNSTON, J.: *Discussion on Physical Chemistry of Steelmaking*, 258
JORDAN, L. AND VACHER, H. C.: *Discussion on Gases Extracted from Iron-carbon Alloys by Vacuum Melting*, 440
JOSEPH, T. L.: *Discussions: on Iron-ore Sinter*, 66, 67
on Manganese Ore by the Bradley Process, 83
JOSEPH T. L. AND FURNAS, C. C.: *Blast-furnace Filling and Size Segregation*, 98
JOSEPH, T. L. AND WOOD, C. E.: *Effect of Barium Oxide on the Desulfurizing Power of Blast-furnace slags*, 126

K

KING, C. D.: *Basic Open-hearth Yields*, 197; *Discussion*, 232
Discussion on Physical Chemistry of Steelmaking, 235 et seq.
KINNEY, C. L.: *Discussion on Physical Chemistry of Steelmaking*, 237, 240

KINNEY, S. P. AND FURNAS, C. C.: *Gas-solid Contact in the Shaft of a 700-ton Blast Furnace*, 84
KINZEL, A. B.: *Discussions: on Diffusion of Iron Oxide from Slag to Metal in the Open-hearth Process*, 300, 302
on Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron, 313, 314, 315, 318, 319
on Physical Chemistry of Steelmaking, 250, 251, 252, 255
KINZEL, A. B. AND EGAN, J. J.: *Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron*, 304

L

Laterite. *See* Iron Ores.
LE BRUN, M.: *Discussion on Metallic Electrodes for Cast-iron Arc Welding*, 158
Luxemburg: iron ore, reserves, 23

M

MACKENZIE, J. T.: *Discussion on Physicial Chemistry of Steelmaking*, 242
Magnetite in sinter, structure, 47
Manganese Ore by the Bradley Process (ZAPFFE) 68; *Discussion*, 82
Manganese ore: Bradley process of making, 68
Manganese sinter: Bradley process, 68
Manganese steel. *See* Steel, Manganese.
Martensite, composition, 365
MCCAUGHEY, W. J.: *Discussion on Physical Chemistry of Steelmaking*, 244, 246
MCKEE, A. G.: *Discussion on Blast-furnace Filling and Size Segregation*, 124
MCKUNE, F. B.: *Discussion on Physical Chemistry of Steelmaking*, 238, 239, 255, 257
MEHL, R. F.: *Discussion on Gamma-alpha Transformation in Pure Iron*, 368
MEISSNER, C. E.: *Discussion on Basic Open-hearth Yields*, 232
Metallic Electrodes for Cast-iron Arc Welding (SATOH) 144; *Supplement*, 161; *Discussion*, 158
Mexico: iron ore, reserves, 19
Models: blast-furnace experiments, 100

N

New Development in Wrought Iron Manufacture (ASTON) 166; *Discussion*, 176
Newfoundland: iron ore, reserves, 18, 38
Nitrogen: relation to blue heat phenomena in iron and dispersion hardening in system iron-nitrogen, 446

O

Open-hearth furnace, basic. *See* Basic Open-hearth Furnace.
Open-hearth Operation from the Chemical Viewpoint (HERTY) 260

P

Physical Chemistry of Steelmaking (ROUND TABLE) 233
Pig iron: classification for basic open hearth, 262
dirty, causes, 179
effect of high manganese on sulfur content, 240
irregular operation of blast furnace detrimental, 195
oxides, unreduced, elimination in basic open hearth, 179
silicates in, 185
silicates affect finished steel, 195
silicon, effect in basic open-hearth, 262
silicon content, 186
silicon content influence on removal of sulfur or phosphorus from steel, 235
POLUSHKIN, E. P.: *Discussion on Gamma-alpha Transformation in Pure Iron*, 361
Pure Iron and Allotropic Transformations (YENSEN) 320; *Discussion*, 333
PUTNAM, W. P.: *Discussions: on Iron-ore Sinter*, 66
on Manganese Ore by the Bradley Process, 82

R

READ, T. T.: *Discussion on Foreign Iron Ores*, 36
Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-nitrogen (DEAN, DAY AND GREGG) 446
RICHARDS, F. B.: *Discussion on New Development in Wrought Iron Manufacture*, 177
RIDDELL, J. M.: *Discussion on Iron-ore Sinter*, 66
ROGERS, B. A.: *Change in Microstructure of Iron at A_3 Transformation Point* 370; *Discussion*, 381
Russia: iron ore, reserves, 36

S

Sarbey furnace: description, 305
SATOH, S.: *Metallic Electrodes for Cast-iron Arc Welding*, 144; *Supplement*, 161
SAUVEUR, A.: *Discussion on Pure Iron and Allotropic Transformations*, 333
SAUVEUR, A. AND CHOU, C. H.: *The Gamma-alpha Transformation in Pure Iron*, 350; *Discussion*, 369
SCHWARTZ, G. M.: *Iron-ore Sinter*, 30
Scrap metal: basic open-hearth production, 197, 211, 215
SIMMONS, R.: *Discussion on Physical Chemistry of Steelmaking*, 238
Sinter: benefit in blast furnace, 66, 121
iron ore, microscopic study, 43
structure and composition, 30, 59
Sintering: cause of bonding, 62
cost cut by manipulation of raw materials, 121
Sintering iron ore, fundamental reactions, 39
resulting minerals, 39
SOSMAN, R. B.: *Discussion on Physical Chemistry of Steelmaking*, 245, 246
Spain: iron ore, reserves, 24
Steel: effect of oxide inclusions, 282
free iron oxide content, 283
Hadfield's manganese, studies with high-power microscope, 382

Steel, manganese: annealing at low temperatures, effect, 406
Hadfield's, studies with high-power microscope, 382
slip lines, 384, 385
dendritic structure, 394
grain size affected by transformation, 414
pearlitic threads, 400
tensile properties affected by double heat treatment, 425
Steelmaking (*See also* Basic Open-hearth Practice):
CO pressure, 249
carbon elimination, rate, 248, 274
diffusion of iron oxide from slag to metal in open hearth, 284
effect of high manganese on fluidity of slag and elimination of silicate impurities, 240, 267
elimination of unreduced oxides of pig iron in the open hearth, 179
equilibrium of system iron oxide-carbon in molten iron, experimental data, 304
foaming, causes and correction, 237, 265
gases given off from ingots during solidification, 254, 278
influence of silicon content of pig iron on removal of sulfur or phosphorus from steel, 235, 262
iron oxide, effect on quality of rimming steels and killed steels, 246, 272
iron oxide in slag, form, 243, 271
reduction, 246, 272
ladle reactions, 193, 253, 275
oxide content of heat in open hearth vs. that in electric furnace, 317
physical chemistry, round table discussion, 233
pig iron from irregular blast-furnace operation is detrimental, 196
pig iron silicon content, influence on removal of sulfur or phosphorus from steel, 235
piping, 281
sampling molten metal, 316
silicates high when high in pig iron, 195
slag action in ladle, 193, 253, 275
Studies of Hadfield's Manganese Steel with the High-power Microscope (HALL) 382
STYRI, H.: *Discussions: on Diffusion of Iron Oxide from Slag to Metal in the Open-hearth Process*, 301, 302
on Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron, 314, 318
on Physical Chemistry of Steelmaking, 253
Sweden: iron ore, reserves, 24

T

THACKRAY, G. E.: *Discussion on Physical Chemistry of Steelmaking*, 243, 253

U

United States: iron ore, imports, 33
reserves, 16, 33, 36, 38
Unreduced Oxides in Pig Iron and Their Elimination in the Basic Open-hearth Furnace (HERTY AND GAINES) 179

V

VACHER, H. C. AND JORDAN, L.: *Discussion on Gases Extracted from Iron-carbon Alloys by Vacuum Melting*, 440
Venezuela: iron ore, reserves, 21

W

WATERHOUSE, G. B.: *Foreword*, 5
Discussions: on Diffusion of Iron Oxide from Slag to Metal in the Open-hearth Process, 299, 302
on Experimental Data on the Equilibrium of the System Iron Oxide-carbon in Molten Iron, 316, 317, 318
on Foreign Iron Ores, 38
on Iron-ore Sinter, 66
on Manganese Ore by the Bradley Process, 83
on New Development in Wrought Iron Manufacture, 176
on Physical Chemistry of Steelmaking, 242, 255
Welding: arc, cast iron, fusion of electrode retarded by barium carbonate in coating, 144
cast iron, fusion of electrode affected by elements in coating, 161
cast iron with coated wrought-iron electrodes, 144, 161
WOOD, C. E. AND JOSEPH, T. L.: *Effect of Barium Oxide on the Desulfurizing Power of Blast-furnace Slags*, 126
Wrought iron: Byers new process, 166
manufacture, essential steps in process, 167

Y

YAP CHU-PHAY: *Discussion on Pure Iron and Allotropic Transformations*, 344
YENSEN, T. D.: *Pure Iron and Allotropic Transformations*, 320; *Discusson*, 346
Discussion on Physical Chemistry of Steelmaking, 256, 258

Z

ZAPFFE, C.: *Manganese Ore by the Bradley Process*, 68; *Discussion*, 82, 83
ZIEGLER, N. A.: *Gases Extracted from Iron-carbon Alloys by Vacuum Melting*, 428; *Discussion*, 444
Discussion on Change in Microstructure of Iron at A_3 Transformation Point, 380